

ANALYTICAL ABSTRACTS

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2870 Ethylenediaminetetra-acetic acid as a masking agent in analytical chemistry. H. Flaschka (Nat. Res. Centre, Dokki-Cairo, Egypt). *Angew. Chem.* 1957, 69 (22), 707-712.—A review is presented of the use of EDTA as a masking agent in pptn., qual. detection of trace elements, photometric determinations and titrations. N. E.

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2868 The reduction and presentation of experimental results. British Standards Institution (2, Park St., London). B.S. 2846:1957, 43 pp.—Exact and approximate methods are given for the calculation of the mean and standard deviation (together with their confidence limits) of a set of experimental results. The construction of histograms and frequency curves is described in some detail; control charts are only briefly mentioned. Rounding errors and the underlying assumption of normality are discussed, and the Standard includes a short glossary of statistical terms. B. J. WALBY

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cation with a complexing agent is measured with Ni^{2+} , Co^{2+} , Cu^{2+} and UO_2^{2+} titrated against salicylaldehyde. The equilibrium constant (K_R) of the titration reaction is calculated directly and this is related to the required stability constant (K) by $K = K_R/K_D$, where K_D is the acid dissociation constant of the complex. The mean values for the stability constants of salicylaldehyde complexes determined from titrations in both directions are— Ni^{II} complex 9-31, Co^{II} 8-45, Cu^{II} 12-57, and UO_2^{2+} complex (one direction only) 12-83.

E. J. H. BIRCH

2874. Differential electrolytic potentiometry. II. Precision and accuracy of applications to redox titrimetry. E. Bishop (Washington Singer Lab., The Univ., Exeter, England). *Analyst*, 1958, **83**, 212-222.—The precision and accuracy of differential electrolytic potentiometry applied to a random assortment of redox titrations have been examined. Among the applications of the method to the electron-transfer reactions reported, two types of titration graph are found, *viz.*, reactions in which both oxidant and reductant are reversibly electrolysed, and those in which the oxidant is not reversibly electrolysed. The apparatus and the procedure are described and results of the titrations for several reactions are quoted with examples of the graphs obtained. The accuracy compares well with that of classical potentiometric methods, and the precision, owing to the sharpness of the end-points, is improved 2 to 10-fold.

A. O. JONES

2875. Coulometry and the coulomb as a universal primary standard. P. S. Tutundžić (Technol. Fac., Univ., Belgrade, Yugoslavia). *Anal. Chim. Acta*, 1958, **18** (1-2), 60-68 (in German).—Some examples of the wide application of coulometry listed are—determination of the hardness of water, production of oxidising agents such as MnO_4^- , IO_4^- and $\text{S}_2\text{O}_8^{2-}$, $\text{Cr}_2\text{O}_7^{2-}$ *in situ*; metallometry, where metal ions generated at the anode are used to determine anions with which they form sparingly soluble compounds, and which might possibly be used preparatively in the separation of isomers; the study of the kinetics of complex formation; coulometric buffering. The use of coulometric titrations permits an accuracy not normally attained in volumetric analysis, and also a greater reliability. If only because of the large number of standards of varying reliability in the different fields of analytical chemistry, the introduction of the coulomb as the universal standard for volumetric, potentiometric, amperometric and conductimetric analysis would be justified.

J. H. WATON

2876. Spectrophotometry in industrial chemistry. H. W. Thompson (Oxford Univ., England). *Chim. Anal.*, 1957, **39** (12), 445-448.—Recent developments in spectroscopic technique in the infra-red, and its uses for the determination of molecular structure, for qualitative and quantitative analysis of mixtures, for continuous process control, and for the investigation of reactivity and other molecular properties are briefly discussed. The principle of the method, depending on the measurement of the position, intensity, and degree and type of polarisation of the absorption bands characteristic of the substance under examination, is discussed and reference is made to several applications.

R. E. ESSERY

2877. Analytical curves in isotopic spectral analysis. A. R. Striganov (Commission for Spectroscopy, Acad. of Sci., USSR, Moscow). *Appl. Spectroscopy*, 1957, **11** (4), 145-147.—A simple relationship is deduced between the intensities of lines of different isotopes of heavy elements and their relative concentrations. The deduction is confirmed experimentally by measurements on absorption-free lines of the isotopes ^{235}U and ^{238}U , after suitable corrections for background and mutual superposition effects have been made. For lighter elements the relationship is complicated by effects produced by differences in the physical properties of the isotopes. The theoretical equation is confirmed by measurements on the spectra of gaseous mixtures of hydrogen and deuterium.

P. T. BEALE

2878. Some recent developments in polarography. G. W. C. Milner (A.E.R.E., Harwell, England). *J. Polarographic Soc.*, 1958, **1** (1), 2-4.—Introduction of the square-wave polarograph extended the scope of this method to trace analysis with concn. in the range 10^{-4} to $10^{-7} M$ of many reversibly reduced substances. Analytical applications are indicated, and methods of obtaining increased sensitivity are discussed.

H. F. W. KIRKPATRICK

2879. Precision polarography. Å. Bresle (Boliden Mining Co., Skelleftehamn, Sweden). *Sci. Tools*, 1957, **4** (3), 33-36.—The accuracy of values for element concn. as obtained by the conventional treatment of a polarogram is discussed. Possible sources of error are (i) calculation of the true diffusion current (errors of 1 to 3% can arise), and (ii) deviations from assumed linearity of the curves of potential *vs.* condenser or diffusion current. Greater accuracy is attainable when the drop time is kept const. through the whole polarogram by a simple mechanical device (*cf.* Wählin and Bresle, *Acta Chem. Scand.*, 1956, **10**, 935).

W. J. BAKER

2880. Mass spectrometry in chemical research and production. F. W. McLafferty (Spectroscopy Lab., Dow Chemical Co., Midland, Michigan, U.S.A.). *Appl. Spectroscopy*, 1957, **11** (4), 148-156.—Various applications of mass spectrometry are described. They include the quantitative analysis of light oils and continuous plant-stream analysis, such as argon in the recycle nitrogen stream of an ammonia plant and nitrogen and oxygen in finished argon in an air-separation plant. Qualitative analysis is possible by reference to spectra of known pure substances recorded in a card index. Molecular structures may be investigated, particularly by the introduction of stable isotopes. (64 references.)

P. T. BEALE

2881. Paper-electrophoretic separation of inorganic anions. M. Lederer (Inst. du Radium, Lab. Curie, Paris, France). *Anal. Chim. Acta*, 1957, **17** (6), 606-607 (in English).—The movements of 31 inorganic anions, with 2% ammonium carbonate soln. as carrier electrolyte, and at a potential of 150 V for 1 hr. in a moist chamber, are recorded. All the spots were placed 1.5 cm from the border of the cathode compartment, and chromate was used as reference spot. Liquid flow due to evaporation and lack of saturation was appreciable. Mixtures of ClO_3^- , BrO_3^- and IO_3^- could be separated, also those of BrO_3^- , IO_3^- and IO_4^- , but periodate is partly reduced, and also

separated into two spots which move very little. Other separations, which have been previously achieved with other electrolytes, were of borate from most of the anions tested, arsenite from arsenate, and selenite from tellurite.

R. E. ESSERY

2.—INORGANIC ANALYSIS

2882. Determination of micro quantities of certain metals by means of dithizone. C. P. van Dijk and F. M. Slothouwer (Rijksinst. voor de Volksgezondheid te Utrecht, Holland). *Chem. Weekbl.*, 1957, **53** (52), 704-708.—It is claimed that, for the determination of traces of metals in body fluids and foodstuffs, the titrimetric method with dithizone is more accurate and reliable than any others described in the literature. Details are given for the prep. of the reagents and solvents required, and the procedures for the determination of micro amounts of Pb, Bi, Zn, Cd, Cu, Hg and Au. Attention is drawn to the possible loss of traces of metal from neutral or alkaline aq. soln. by adsorption on to the walls of glass vessels, and an example is quoted.

P. HAAS

2883. Polarographic determination of impurities in semi-conductor materials. F. A. Pohl (AEG Forschungs-Inst., Beleecke a.d. Mohne, Germany). *J. Polarographic Soc.*, 1958, **1** (1), 8-10.—Micro-methods of preparing soln. for analysis of costly or rare materials are described. Diode gold wire (10 to 50 mg) is dissolved in aqua regia; the dried residue is dissolved in 3 N HBr (1 ml) and the gold is extracted with diisopropyl ether (3 × 1 ml). The acid soln. is dried, fumed off with HClO₄ (0.2 ml), and the residue is dissolved in 6 N aq. NH₃ (0.2 ml) and polarographed. Determination of trace metals in selenium (1 g) is also described, the traces being separated into two groups by micro-extraction. Stress is laid on the need for purity of reagents and cleanliness of apparatus and working conditions.

H. F. W. KIRKPATRICK

2884. Interferences of three elements in flame photometry. Chromium-cobalt-manganese system. F. Burriel-Martí, J. Ramírez-Muñoz and M. C. Asunción-Omarrementería (Fac. of Sci., Univ., Madrid, Spain). *Anal. Chim. Acta*, 1957, **17** (6), 545-558 (in English).—A method of correction for the mutual interferences of three elements is described, using "ponderal ratios." In a two-element system, if R_p is the ponderal ratio, $[I.E.]$ and $[A.E.]$ are the concn. of interfering and analysis elements, respectively, as found in the photometer, $[A.E.]$ is the known concn. of analysis element in a standard sample, and F_e is the factor to convert observed to true concn., then $R_p = [I.E.] \times ([I.E.] + [A.E.]) / [A.E.]$; $F_e = [A.E.] / [I.E.]$; $F_e = m \log R_p + b$. When the last equation is represented graphically, a series of straight lines is obtained, one for each value of $[A.E.]$, and when the lines are obtained from a series of known mixtures they may be used to obtain the correction factor F_e to be applied to the measurements of the unknown. The method is described of extending this treatment to a system of three elements when the behaviour of the several two-element systems of which it is composed is known. Results for the system Cr - Co - Mn are given for aq. and acid soln.,

and a comparison between flame-photometric and chemical results is given for two ferrous alloys. The interpretation of the F_e vs. R_p graphs is discussed.

R. E. ESSERY

2885. The application of vacuum ultra-violet techniques to the continuous monitoring of trace concentrations of water in several gases. W. R. S. Garton, M. S. W. Webb and P. C. Wildy (Imperial College, London). *J. Sci. Instrum.*, 1957, **34** (12), 496-500.—The 1216-Å Lyman α -line is excited by a 20 Mc/s electrodeless discharge in hydrogen. The radiation passes through an absorption cell fitted with lithium fluoride windows on to a photomultiplier insensitive to wavelengths longer than 1400 Å.

G. SKIRROW

2886. Determination of the oxygen content of sodium metal by the butyl bromide method. L. E. Smythe and H. J. de Bruin (Australian A. E. Commission, Res. Estab., Sutherland, N.S.W., Australia). *Analyst*, 1958, **83**, 242-244.—The accuracy of the determination of the oxygen content of sodium by the butyl bromide method depends on recognition of the end-point when the bromide-oxide mixture is dissolved in water and titrated with dil. HCl, and this recognition is subject to considerable error even when a glass electrode indifferent to the presence of Na⁺ is used. The low solubility of NaBr in ethanol suggested the use of this as a solvent instead of water, and a statistical survey was made of the accuracy of detecting the end-point (to methyl red) in 10 ml of 0.002 N NaOH diluted to 30 ml with water-ethanol mixtures, saturated with NaBr, and with a progressive increase in the water content. It was found that the titration can be made with precision and accuracy if the Na₂O - NaBr mixture is allowed to react with the requisite vol. of a 90 to 95% v/v ethanol-water mixture when following the specified procedure.

A. O. JONES

2887. Potentiometric determination of sodium ions by means of a glass electrode with a sodium function. V. É. Goremýkin and P. A. Kryukov (Hydrochem. Inst., Acad. Sci., USSR). *Izv. Akad. Nauk, SSSR, Otdel. Khim. Nauk*, 1957, (11), 1387-1389.—The activity coeff. of Na⁺ is approx. the same in soln. of NaCl and Na₂SO₄ provided that the ionic strength is < 0.05. With natural waters the coeff. can be calculated from the equation of Harned and Owen provided that the sum of the equiv. concn. of Ca²⁺ and Mg²⁺ does not exceed 6 times the equiv. concn. of Na⁺. A glass electrode with a sodium function (Shul'ts, *Uch. Zap. Leningrad. Gos. Univ., Ser. Khim. Nauk*, 1953, **13**, 80) can be used to determine the activity of Na⁺ in natural waters and by calculation with use of the activity coeff. the concn. of Na⁺ can be found. If the pH is < 6, the soln. is neutralised to neutral red indicator. (Cf. Kryukov et al., *Anal. Abstr.*, 1957, **4**, 713.)

G. S. SMITH

2888. Chromatographic separation of the alkali metals, the alkaline earths and the rare earths. J. Fouarge and J. Fuger (Univ. de Liège, Belgium). UNESCO/NS/RIC/52, 1957, 18 pp. (in French).—Good separations of Cs and Rb have been achieved by elution from a cellulose column with phenol equilibrated with 2 M HCl. Separation of carrier-free Cs from irradiated U was carried out by the use of a strip of paper and the same solvent; H₂O₂ was used to eliminate interference from Zr and Nb.

Lithium, Na and K have been separated by elution from a cellulose column with methanol containing a few per cent. of HCl. Strontium and Ba have been separated by elution with a mixture of methanol, ether and HCl (15:5:1, by vol.) till the Sr was recovered, and then with a mixture of methanol and HCl (20:1, v/v) to recover the Ba; excellent separations of Ba and Ra were achieved by using the second mixture. Yttrium and La have been successively eluted from Dowex 50 (NH_4^+ form) with 0.01 M EDTA at pH 6, followed by Sr and Ba at pH 8. Calcium, Sr, Ba and Ra were similarly eluted from the resin, the first two at pH 7.4 and the second two at pH 9. Very strict control of conditions was required to ensure reproducible elutions of Y, Eu, Pm and Ce from Dowex 50 (NH_4^+ form) with 0.025 M EDTA in the pH range of 3.05 to 3.65; better results were achieved by eluting with a soln. at pH 6.82 that was 0.025 M with respect to EDTA and 0.05 M with respect to $\text{Zn}(\text{NO}_3)_2$ from a column of resin in the Zn form. G. J. HUNTER

2889. Fast Sulphon black F as an indicator for the EDTA titration of copper. R. Belcher, R. A. Close and T. S. West (Birmingham Univ., England). *Chem. & Ind.*, 1957, (51), 1647.—If a 0.5% aq. soln. of Fast Sulphon black F (C.I. No. 306) is used as indicator, the addition of an excess of EDTA to a moderately conc. soln. of Cu^{2+} , in the presence of aq. NH_3 , produces a sharp change of colour from pale blue to bright green. The reaction is specific for Cu^{2+} , so that 10 ml of the Cu soln. (≈ 0.02 M) can be titrated directly with 0.02 M EDTA in the presence of 1 ml of conc. aq. NH_3 and 2 drops of indicator soln. Trace metals do not interfere, but metals that form sol. complexes with EDTA at the pH of titration should be removed or masked.

W. J. BAKER

2890. Colorimetric determination of copper by the use of zinc diethyldithiocarbamate. Yoshimasa Tanaka and Kazuo Ito (Pharm. Fac., Kumamoto Univ., Oe-cho, Kumamoto). *Japan Analyst.*, 1957, **6** (11), 728-731.—The use of Zn diethyldithiocarbamate (I) in CCl_4 (0.02%) for the extraction of Cu ($< 1.5 \mu\text{g}$ per ml) was studied with reference to the elimination of interference from other metal ions. Iron, Co, Ni and Bi give a similar, weaker coloration, but the positive error arising is much less than that when the sodium salt is used. The separation of Cu from interfering ions is best effected with dithione in CCl_4 . The org. layer containing 3 to 40 μg of Cu is extracted with aq. Zn di(hydroxyethyl)-dithiocarbamate soln. (0.005%, ≈ 25 ml) (this aq. soln. is not stable enough for colorimetry), and the aq. layer (pH 3 to 4) is then extracted with a few portions of the CCl_4 soln. of I (≈ 3 ml each). The extract is made up to 20 ml and the extinction is measured at 420 m μ .

K. SAITO

2891. Determination of copper by means of short-circuit limited-potential coulometry. Soichiro Musha and Ichihiko Niwa (Fac. of Engng, Osaka Prefectural Univ., Sakai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (11), 1672-1676.—Coulometry of Cu was studied by the measurement of the current in the internal electrolysis in H_2SO_4 . An apparatus was devised for the following cell: saturated cadmium amalgam (5 mg) | M CdSO_4 in 0.1 N H_2SO_4 || 0.1 N H_2SO_4 | Cu. The sample soln. (5 to 20 mg of Cu in 0.1 N H_2SO_4) is added to the electrolytic soln. after the background current ($\approx 0.2 \mu\text{A}$) has become constant. The current is measured at regular intervals during the electrolysis

(5 hr. for 20 mg) and the total current is calculated from the current-time diagram. Dissolved O must be removed with a current of N.

K. SAITO

2892. Electrochromatography in the separation of ions. III. Separation of silver-group metals. A. K. Majumdar and B. R. Singh (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1957, **17** (6), 541-544 (in English).—The separation of Ag^+ , Hg^{2+} , Pb^{2+} and Ti^+ on Whatman No. 2 paper ($44 \text{ cm} \times 1 \text{ cm}$) with 34 different complex-forming electrolytes was studied. The metals were added as nitrates (15 μg of each ion) and 150 V was applied for 3 hr., the apparatus and technique being as previously described (Majumdar and Mukherjee, *Ibid.*, 1956, **15**, 547; Majumdar and Chakrabarty, *Ibid.*, 1957, **17**, 228). Of the electrolytes studied, the only ones suitable for the complete separation of the four ions from quaternary mixtures were 0.1 N aq. NaCl, KCl or KCN, in which the migration sequence was Hg, Ag, Pb, Ti; and KCN at pH 7.0, in which it was Ag, Hg, Pb, Ti. R. E. ESSERY

2893. Determination of traces of silver in silicate rocks. Hiroshi Hamaguchi and Rokuro Kuroda (Chem. Dept., Fac. of Sci., Tokyo Univ. of Education, Koishikawa). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (11), 1668-1671.—Silver in silicate rocks (0.03 to 0.7 μg per g) is collected by co-pptn. with Te and determined spectrographically, with In as internal standard. The pptn. of Ag with Te is quant. in 1 to 2 N HCl. The working curve (Ag 3280-68 vs. In 3256-09 A) is linear for $< 3 \mu\text{g}$ of Ag, the overall error being $\approx 15\%$. The sample (1 g) is decomposed with HClO_4 and HF by the usual method and dissolved in 2 N HCl (50 ml). The HCl soln. is mixed with telluric acid (2 mg of Te per ml), boiled with SnCl_2 (15% in 2 N HCl) (10 ml) for 15 min. and filtered. The pptd. Te is dissolved in conc. HNO_3 (0.5 ml), mixed with In soln. (10 μg of In per ml of N HNO_3) (1 ml) and NaNO_3 (20 mg per ml) (1 ml) and placed in the crater (diam. 3 mm, depth 2 mm) of a carbon electrode (diam. 5 mm) for an arc discharge (7 amp., 25 sec.).

K. SAITO

2894. Micro-analysis of silver bromide, silver iodide and lead iodide. R. Kuhn and H. Schretzmann (Max Planck Inst. f. Med. Forsch., Inst. f. Chem., Heidelberg). *Chem. Ber.*, 1957, **90**, 554-556.—For the determination of iodine and bromine in AgBr and AgI the silver is pptd. on zinc turnings by boiling an alkaline cyanide soln. After filtration and washing, the cyanide in the soln. is destroyed by heating with H_2O_2 soln. The iodine is then oxidised to IO_3^- by means of Br or the bromine to BrO_3^- by means of NaClO (Belcher *et al.*, *Anal. Abstr.*, 1954, **1**, 2696). The IO_3^- and BrO_3^- are then determined by known methods. In a second method for the determination of Ag in AgI, the soln. in KI is heated with a soln. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and propylenediamine. The complex is filtered off, washed, dried and weighed. A method is described for the determination of iodine in PbI_2 or its complex with tetramethylammonium iodide in which the iodine is distilled from hot conc. H_2SO_4 in a special apparatus (illustrated), oxidised to IO_3^- and determined in the usual way.

S. BAAR

2895. A tracer study on the loss of silver in cupelling with silver-110. Yoshitaka Nakamura and Kenji Fukami (Central Lab., Nippon Mining Co., Karasuyama, Setagaya-ku, Tokyo). *Japan*

Analyst, 1957, **6** (11), 687-690.—Loss of Ag (<2 mg) in the cupelling (30 min.) of a lead button (30 g) was examined at 820°. The percentage loss increases with decreasing amount of Ag (e.g., $\approx 6\%$ for 1.8 mg of Ag, $\approx 10\%$ for 0.5 mg, and $\approx 30\%$ for 0.1 mg). Most ($\approx 90\%$) of the lost Ag is found in the thin layer (≈ 2 mm) of the cupel beneath the silver bead. No significant evaporation of Ag was observed.

K. SAITO

2896. Semi-quantitative determination of a small amount of metal by paper chromatography. II. Determination of gold in the presence of a large amount of copper. Shiro Harasawa and Suehiko Hayano (Fac. of Engng, Yamaguchi Univ., Ube, Yamaguchi Prefecture). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (12), 1707-1709.—When Au ($>2.5 \mu\text{g}$ per ml) and Cu ($<150 \mu\text{g}$ per ml) are developed with a mixture of butanol, HCl and water (4 + 1 + 1, by vol.), Cu exhibits a broad band of $R_F \approx 0.3$ and Au gives a spot of $R_F \approx 0.7$. The latter is detected with *p*-dimethylaminobenzylidenethiodaniline (saturated ethanolic soln.) or benzidine (0.05% in 10% acetic acid), and the approx. amount of Au is estimated by comparison with a series of standard.

K. SAITO

2897. The compounds of gold and palladium with rubeanic acid (dithio-oxamide). Composition, structure and analytical use. M. Bobtelsky and J. Eisenstadter (Dept. of Inorg. and Anal. Chem., Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1957, **17** (6), 579-587 (in English).—With rubeanic acid, Au gives AuR at pH 1 to 3, Au₂R₂ at pH 5 to 7, and Au₃R₃ at pH 8 to 10. At pH 1 to 3, Pd yields Pd₂R₂, in certain cases transformed by excess of reagent into PdR; at pH 7 to 8, Pd₂R₂ is obtained, sometimes converted by excess of reagent into PdR₂. For analysis, stock rubeanic acid soln. (0.004 M in 95% ethanol) is diluted with water to give a working reagent in $\approx 50\%$ ethanol. In the heterometric titration of Au as chloride (1 mg in 20 ml) in mineral or acetic acid soln., the end-point is given by the first point of maximum extinction, corresponding to the quant. formation of AuR, the titration taking 20 to 30 min. In strong ammoniacal soln., the end-point corresponds to Au₂R₂, the titration taking 13 min. With Pd (1 mg as chloride in 20 ml, containing 1 ml each of 0.5 M HNO₃ and 0.5 M NaCl or NH₄Cl) the end-point corresponds to Pd₂R₂, the titration taking 15 min. and the error being <1%. Under other conditions, either more than one critical point is obtained, or the titration time is greatly extended. The properties and structure of the complexes are discussed.

R. E. ESSERY

2898. Spectrographic determination of gold, platinum, palladium and rhodium in low-content materials (ores, slags and waste solutions). D. M. Livshits and S. E. Kashlinskaya (A. P. Zavenyagin Norilsk Mining Metall. Combine). *Zhur. Anal. Khim.*, 1957, **12** (6), 714-717.—For determining concn. of approx. 1 g per ton the sample (5 to 10 g) is first ignited and then treated with some water and formic acid to reduce oxides of Pd, followed by boiling with aqua regia (50 to 60 ml) for 1.5 hr. and two successive evaporations with dil. H₂SO₄. After addition of 15 to 20 ml of conc. HCl and 0.3 g of KClO₃ and heating to remove Cl, the soln. is diluted with water and filtered. The filtrate is treated with CuSO₄ soln. containing 0.1 to 0.2 g of Cu, and the boiling soln. is mixed with a 40% soln. of Na₂S₂O₃ so that Au, Pt, Pd and Rh are co-pptd. with CuS.

The washed ppt. is ignited and reduced with H, and the copper containing the precious metals is fused in a graphite crucible. The material is then excited in a d.c. arc and the lines Au 2675-95, Pt 2659-45, and Pd 2447-91 Å are compared with Cu 2445-0 Å, and the line Rh 3434-89 with Cu 3375-67 Å.

G. S. SMITH

2899. New gravimetric micro-method for the determination of beryllium. T. I. Pirtea and G. Mihail (Lab. Inorg. and Anal. Chem., Univ. "C. I. Parhon," Bucharest, Romania). *Z. anal. Chem.*, 1958, **159** (3), 205-208.—Carefully add pure powdered ammonium carbonate (0.5 to 2 g) to a neutral or slightly acid soln. of the sample (0.5 to 3 ml containing 500 μg of Be) in an Emich micro filter-beaker. To the clear soln. add saturated aq. Co(NH₃)₆Cl₃ soln. (0.5 to 2 ml) and filter after 10 to 30 min. Wash the ppt. with 0.2% Co(NH₃)₆Cl₃ soln. (2 \times 0.5 ml) and with a very dilute soln. of Co(NH₃)₆Cl₃ in 60% ethanol (2 \times 0.4 ml). Dry the ppt. by washing in turn with small portions of abs. ethanol (1 ml) and then abs. diethyl ether (1.5 ml); set the ppt. aside in a vacuum-desiccator for 10 min. and weigh the residue of [Co(NH₃)₆][(H₂O)₂Be₂(CO₃)₂(OH)₂] \cdot 3H₂O. If Fe, Al or Mg is present, use EDTA as masking agent. The determination can be completed in 30 to 90 min.

A. R. ROGERS

2900. Photometric determination of beryllium. U. T. Hill (Inland Steel Co., Indiana Harbor, Ind., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 521-524.—Beryllium in concn. of $>10 \mu\text{g}$ in 25 to 50 ml of soln. can be determined accurately, in the presence of large amounts of Al, Fe, Cu, Ti and mixed oxides, by measuring the extinction of the red complex of Be with Eriochrome cyanine R (cf. *Anal. Abstr.*, 1957, **4**, 415) at 512 m μ and pH 9-8 in a 2-cm cell. Interfering ions are masked by the addition of 0.2% excess of 5% EDTA (disodium salt), 5% Na acetate and, when Cu is present, 10% aq. KCN. The adjustment of pH is made with 10% aq. KOH or NaOH according to the elements present. The method is applicable to metals, alloys and ores.

W. J. BAKER

2901. Study of the system beryllium sulphate-sodium hydroxide-water and its analytical application. [Determination of beryllium in the presence of large amounts of aluminium by means of 8-hydroxyquinoline.] I. V. Tananaev and E. P. Shcheglova (Moscow Engng Physics Inst.). *Zhur. Anal. Khim.*, 1957, **12** (6), 671-676.—Mixtures in various proportions of soln. of BeSO₄ and NaOH were maintained at 25° in an atmosphere of N until the systems were in equilibrium (≈ 2 hr.). The clear soln. were analysed and the results were used to determine the composition of the ppt. With 0.025 M BeSO₄ the effect of increasing amounts of NaOH up to a ratio NaOH:BeSO₄ of 1 is to produce a soluble basic sulphate, viz. (BeOH)₂SO₄. With further increase of NaOH an insoluble basic salt, possibly 9Be(OH)₂.BeSO₄, starts to form and when the ratio is 1.8 all the Be has been pptd. Still further increase in the ratio up to 2.8 causes replacement of SO₄²⁻ in the ppt. by OH⁻. From a ratio of 2.8 (excess concn. of NaOH 0.025 M) to 12.0 (excess concn. of NaOH 0.25 M) the solubility of Be gradually increases. The results are used to effect an almost complete separation of Be from large amounts of Al so that 8-hydroxyquinoline can be used to determine Be by the method of Kolthoff and Sandell (*J. Amer. Chem. Soc.*, 1928, **50**, 1900). The soln. containing

Be and Al, e.g., 0.01 g of Be and 1 g of Al, is treated with NaOH soln. until it is alkaline to phenolphthalein indicator. The soln. (100 to 210 ml) is then further treated with NaOH so that the excess, on the assumption that 1 mol. of NaOH is equivalent to 1 atom of Al, is 0.01 M. After 30 min., during which time the soln. is periodically stirred, the ppt. of $\text{Be}(\text{OH})_2$ containing some of the Al is collected, and after two washings with water is returned to the original beaker, dissolved in HCl, and treated with 8-hydroxyquinoline for the pptn. of the residual Al. After filtration of the soln. the excess of reagent is destroyed by heating with HNO_3 and Be is pptd. with aq. NH_3 . G. S. SMITH

2902. Determination of oxygen in beryllium by the micro vacuum fusion method. E. Booth and A. Parker (U.K.A.E.A., Res. Group, Woolwich Outstation, Woolwich, England). *Analyst*, 1958, **83**, 241-242.—The apparatus, sample preparation, etc., have been previously described (Booth *et al.*, *Analyst*, 1957, **82**, 57). After some difficulty a rod of beryllium with uniform distribution of oxygen was obtained and served as an appropriate reference standard. It was found necessary to add 60 mg of tin foil to the platinum bath both before the addition of any beryllium and together with each sample. This suppresses the evaporation of beryllium. A "fall-off" in apparent oxygen content appears when a long series of expt. is made, and it is thought that 6 to 8 samples are all that can be safely dealt with in one series. With many of the samples examined the spread of results is such that a single determination may not produce a figure representative of the bulk material. This must be attributed to non-uniform distribution of oxygen in the metal. Results with the uniform reference sample repeatedly showed a coeff. of variation of $\pm 8\%$ and this is considered satisfactory. A. O. JONES

2903. Determination of magnesium in aluminium alloys by photometric titration. Teruyuki Kanie (Nagoya Municipal Ind. Res. Inst., Rokuban-cho, Atsuta-ku, Nagoya). *Japan Analyst*, 1957, **6** (11), 711-715.—The use of Chrome azurol S (I) (Wood, *Anal. Abstr.*, 1955, **2**, 1769; Theis, *Anal. Abstr.*, 1955, **2**, 1767) for the photometric titration of Mg with EDTA was studied with triethanolamine (II) for the masking of Al. The Mg-I lake has a max. absorption at 580 m μ , and the extinction decreases linearly with the amount of Mg^{2+} (<1 mg per 50 ml) in an ammonium buffer. No colour change is observed with Ni, Zn, Cu, Ca, Ba, Cr, Mo, Pb, Cd and V, but Mn and Co give a coloration. *Procedure*—Mix the sample soln. (in HCl, containing ≈ 3 mg of Mg) (SiO_2 is filtered off) with 1% II (40 ml) and add NaOH - NaCN soln. (5 g of NaOH and 2 g of NaCN in 100 ml of water) until the ppt. dissolves. Filter and wash the ppt. with 1% NaOH soln. Dissolve the ppt. in 2% HCl (50 ml), add NH_4Cl soln. (10%, 2 ml), aq. NH_3 soln. (5 ml), II (10%, 5 ml) and NaCN (10 mg) and titrate with 0.01 M EDTA in the presence of I (0.1%, 1 ml). K. SAITO

2904. Analysis of mixed oxides of calcium. R. S. Johnston, E. D. Osgood and R. R. Miller (Chem. Div., U.S. Naval Res. Lab., Washington, D.C., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 511-513.—The percentage of CaO_2 , CaO , $\text{Ca}(\text{OH})_2$ and CaCO_3 in preparations of mixed oxides can be determined by heating the sample 1 (g), dried to const. wt. at 110°, at 550° for 1 hr. in *vacuo* in a tube connected to drying and gas-collection bulbs, and then cooling

to $\approx 25^\circ$. The initial and final temp., barometric and manometric pressures, and wt. changes of sample and drying-tubes are recorded, whilst the percentage of Ca in the residue is determined by an oxalate pptn. The percentage of each constituent is then calculated (as shown) from these data. Commercial CaO_2 contains from 2 to 3% of CaO . This pyrolytic procedure is quicker and is claimed to be more accurate than chemical analyses.

W. J. BAKER

2905. A rapid routine analysis of limestone. Torao Sato and Akiji Ikegami (Arai Plant, Dainippon Celluloid Co., Arai, Niigata Prefecture). *Japan Analyst*, 1957, **6** (11), 706-711.—The routine analysis of limestone was modified to decrease the time by 25%. The results agree with those obtained by the ASTM method, and there is a similar standard deviation. The sample (0.2 g) is decomposed with HClO_4 (60%, 0.5 ml) and HCl (1 + 1, 5 ml) and divided into three portions, for EDTA titration of Ca, for EDTA titration of Mg, and for photometry of Fe with nitroso-R salt. Another 0.2 g of the sample is fused with NaOH (2 g) and two aliquots are used for photometry of Si with molybdate and for photometry of Al with 8-hydroxyquinoline in benzene. K. SAITO

2906. Flame-photometric determination of strontium in ores. N. S. Poluektov, M. P. Nikonova, Ts. A. Lelderman and G. S. Lauër (Ukrainian Branch of the State Rare Metals Sci. Res. Inst., Odessa). *Zhur. Anal. Khim.*, 1957, **12** (6), 699-703.—The intensity of the line 460.7 m μ in an air-acetylene flame is measured by means of a photomultiplier and a galvanometer. Methods for preventing the interference of Ca by modifying the preliminary treatment of the sample are described. G. S. SMITH

2907. Indirect photometric micro-determination of barium by precipitation as chromate. With discussion of errors. J. Agterdenbos (Lab. Anal. Chem., Univ. Amsterdam, Holland). *Z. anal. Chem.*, 1958, **159** (3), 202-205.—Mix the sample (5 ml containing 0.2 to 5 mg of Ba) with acetate buffer (pH 6) (1 ml), warm, add an excess of 10% K_2CrO_4 soln. and allow to cool during 1 hr. Filter through asbestos, wash the ppt. with very dil. aq. NH_3 , dissolve in 3 N HCl (2 \times 5 ml) and measure the extinction at 350 m μ in 1- or 4-cm cuvettes. For a sample that contains 50 to 500 μg of Ba, add borate buffer (pH 8) and 0.2% K_2CrO_4 soln. (1 ml); to a soln. of the chromate in 0.2 N HCl add a 1% soln. of diphenylcarbazide in acetone (1 ml) and measure the extinction at 540 m μ . The presence of Sr (<35 μg) or of Ca (<150 μg) does not interfere with the determination of 350- μg amounts of Ba. The coeff. of variation is 0.5 or 1.0% if the chromate colour is measured; 3% if the chromate - diphenylcarbazide colour is measured. A. R. ROGERS

2908. New method for the separation of barium, strontium, calcium and magnesium by paper chromatography. F. Modreanu, S. Fişel and A. Carpov (Inst. Chim. Acad. R.P.R., Jassy, Romania). *Naturwissenschaften*, 1957, **44** (23), 615.—The propionates of these metals are obtained by ion exchange from columns of Amberlite IRA-400. The chromatograms are run on acid-washed Whatman No. 1 strips, 32.5 cm long. The tank is equilibrated with the solvent mixture ethanol-water-propionic acid-aq. NH_3 (20:2:1:1) 24 hr. before use, then 2 to 10 μl of a 0.1 M soln. of the

metals is spotted on the paper and developed in the solvent for 6 to 7 hr. After drying, the chromatogram is sprayed successively with Na rhodizonate for Ba and Sr, quinalizarin in 0.1 N NaOH for Mg, and gallacetophenone as reagent for Ca. The system gives very good separation with the following R_F values—Ba 0.23, Sr 0.56, Ca 0.82 and Mg 0.93. E. KAWERAU

2909. Examination of ferrocyanide titration of zinc in ores. Hitoshi Kamada, Shigeru Serizawa and Teruko Tawarada (Tokyo Res. Lab., Mitsui Metal Mining Co., Shimomoguro, Tokyo). *Japan Analyst*, 1957, **6** (11), 733-735.—JIS (Japan Ind. Standard), BMC (British Metal Corp.) and Knight's method for volumetric analysis of Zn in ores were examined spectrographically and radiochemically with ^{65}Zn . The main source of error for the first method appears to be the use of a large amount of NH_4Cl in the titration, that for the second is the co-pptn. of Zn with the hydroxides of Fe, Mn, etc., and that for the last the incomplete pptn. of ZnS . K. SAITO

2910. Co-precipitation of zinc, cadmium and mercury with anthranilic acid. I. M. Korenman and M. N. Baryshnikova (N. I. Lobachevskii Gorki State Univ.). *Zhur. Anal. Khim.*, 1957, **12** (6), 690-694.—Co-pptn. at pH values too low for the pptn. of the anthranilates of Zn, Cd and Hg is studied. Various amounts of Na anthranilate soln. are added to soln. containing ^{65}Zn , ^{115}Cd and ^{203}Hg at different pH values and the amount of metal pptd. is determined as a function of the amount of anthranilic acid and pH. With 100 mg of anthranilic acid and at pH 0.65 almost complete pptn. of 25 μg of Cd occurs. Under similar conditions the amount of co-pptn. decreases in the order $\text{Zn} > \text{Cd} > \text{Hg}$. G. S. SMITH

2911. Determination of metal ions by means of their oxalates. IX. Determination of cadmium. Kyozo Kawagaki (Fac. of Engng, Niigata Univ., Nagaoka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (11), 1562-1565.—Cadmium (5 to 100 mg) is quant. pptd. by >5 ml of 0.5 N ammonium oxalate in 50 ml within 24 hr. The presence of acetic acid reduces the time taken for pptn. (e.g., <1 hr. when the concn. of acetic acid is >11 N). Chloride and $(\text{NH}_4)_2\text{SO}_4$ retard the pptn. The ppt. is washed with 50% ethanol and either weighed as CdC_2O_4 or titrated with KMnO_4 in dil. H_2SO_4 .

IX. Determination of magnesium. Kyozo Kawagaki. *Ibid.*, 1957, **78** (11), 1565-1568.—Magnesium (<50 mg) is quant. pptd. as oxalate in $>70\%$ acetic acid by 15 ml of 0.5 N ammonium oxalate within 1 hr. The ppt. is washed with 30% ethanol and either weighed as MgC_2O_4 or titrated with KMnO_4 in dil. H_2SO_4 soln. No interference results from K^+ , Na^+ , NH_4^+ , SO_4^{2-} , NO_3^- or Cl^- . K. SAITO

2912. Determination of mercury in brine, sodium hydroxide and hydrochloric acid. Masami Suzuki and Shizo Hirano (Dept. of Applied Chem., Fac. of Engng, Nagoya Univ., Chikusa-ku). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1957, **60** (7), 869-872.—The extinction (at 372 $m\mu$) of mercury reineckate (I) in an aq. suspension containing poly(vinyl alcohol) (II) obeys Beer's law for 5 to 50 μg of Hg per 50 ml. This suspension is stable for 3 hr. at room temp. No interference results from <10 mg of Mg, Ca, Zn, Mn, Al, As^{III} , As^V , Br^- , NO_3^- , ClO_3^- and SO_4^{2-} , <5 mg of Ni and Co,

and <0.1 mg of Cu and Cd. For the separation of Hg from interfering ions such as Pb^{2+} , I^- , Cl^- and Fe^{3+} , Hg is pptd. with SnCl_2 in 2 N HCl, together with Se. *Procedure*—Add enough 12 N HCl to brine to produce 100 to 150 ml of 2 N HCl soln. Warm on a water bath with H_2SeO_3 soln. (0.75 mg per ml, 2 ml) and SnCl_2 soln. (10% in 2 N HCl, in slight excess to the Se) and filter. Chlorine and ClO^- in the sample are thus reduced to Cl^- . Wash the residue with HCl (1 + 4) and water; dissolve it in HCl (12 N, 1 ml) containing a small amount of KClO_3 . Pass air into this soln. to expel chlorine, add M NaCl (10 ml), II soln. (2%, 10 ml) and water (total vol. ≈ 45 ml) and make up to 50 ml with I (1% in 0.03 N HCl) (2 ml). Measure the extinction after 5 min. Sodium hydroxide soln. (50 ml) is neutralised with 12 N HCl, diluted to 250 ml and a 25 to 50-ml portion is treated similarly. For the analysis of HCl, the sample (2 to 100 ml) is diluted to give a 2 N soln. and an aliquot is treated similarly. K. SAITO

2913. Analytical studies of boron. VI. Determination of boron using ion-exchange resin. Satoru Muto (Kiri Coll. of Technol., Gunma Univ., Japan). *Bull. Chem. Soc. Japan*, 1957, **30** (8), 881-885 (in English).—The soln. is freed from other ions by ion exchange, and the H_3BO_3 is determined by titration or colorimetrically. The sample is decomposed by heating under reflux with a slight excess of 6 N HCl, or by fusion with Na_2CO_3 and dissolution of the melt in 6 N HCl. After being made up to 50 to 100 ml with water, the soln. is passed through successive columns of Amberlite IR-120 (H form) and Amberlite IRA-400 (Cl form), which do not adsorb any B. For milligram amounts of B, the eluate is analysed by an improved Foote's titration (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 39). A portion containing 1 to 5 mg of B is diluted to 100 ml and neutralised to p -nitrophenol (1 drop of 0.1% in ethanol) with N NaOH. After adding 1 drop of N HCl, the soln. is boiled under reduced pressure till the yellow colour re-appears, treated with another drop of HCl and boiled for a further 3 min. The soln. is cooled, the yellow colour is just restored with 0.05 N NaOH, then 2 g of mannitol and 5 drops of phenolphthalein (0.1% in ethanol) are added, and the H_3BO_3 is titrated to a brownish-yellow colour with 0.05 N NaOH. The error is ± 0.02 mg on 1 to 22 mg of B. For microgram amounts of B, the eluate is determined colorimetrically with acetone-curcumin. A portion containing 1 to 5 μg of B is evaporated with 0.2 g of Na_2CO_3 , acidified with 2 ml of HCl-oxalic acid reagent (1 vol. of distilled 6 N HCl to 4 vol. of satd. oxalic acid), and evaporated at 55° , continuing the heating for 30 min. after dryness. Acetone-curcumin soln. is added, the product is dissolved in acetone, centrifuged, and measured at 520 $m\mu$. The error ranges from ± 0.01 to 0.1 μg on 1 to 11 μg of B. Some results are given for rock samples, with and without known additions of B. A. B. DENSHAM

2914. Complexometric titrations (chelatorimetry). XXXV. Indirect determination of aluminium with xylenol orange. M. Houda, J. Körbl, V. Bažant and R. Přibil (Dept. of Org. Technol., Acad. Sci., Prague). *Chem. Listy*, 1957, **51** (12), 2259-2265.—In this indirect determination, the excess of EDTA (disodium salt) (I) is titrated with $\text{Pb}(\text{NO}_3)_2$, ZnSO_4 or $\text{Th}(\text{NO}_3)_4$. For each modification the pH range must be maintained. The alkaline earths and large amounts of alkaline salts do not interfere. *Titration with $\text{Pb}(\text{NO}_3)_2$* —To the slightly acid soln.

of the aluminium salt add an excess of 0.05 M **I** and, when a large amount of neutral salts is present, heat, and then cool. Dilute to 100 ml with H_2O , add 1 to 3 drops of xylene orange (**II**), then hexamine until the bright yellow colour of **I** is less intense, and titrate with 0.05 M $Pb(NO_3)_2$ to a red-violet colour. Titration with $ZnSO_4$.—The procedure is similar to that described above; a sufficient excess of hexamine must be used. Titration with $Th(NO_3)_4$.—To the sample (1.5 to 2.5 mg of Al) add 5.00 to 20.00 ml of 0.05 M **I**, boil when neutral salts are present, then cool, neutralise, add 5 to 10 ml of acetate buffer soln. (pH 3-6), dilute to 100 ml with H_2O , add **II** and titrate with 0.05 M $Th(NO_3)_4$. Manganese does not interfere.

J. ZÝKA

2915. Conductimetric determination of aluminium. G. B. Pasovskaya (Turkmen Med. Inst., Ashkhabad). *Zhur. Anal. Khim.*, 1957, **12** (6), 760-761.—The method is based on the addition of excess of Na oxalate soln. in the presence of (a) methyl violet soln. to hinder adsorption of ions on the ppt. to be formed, and (b) Ca oxalate to improve crystallisation, and conductimetric titration with $Ca(NO_3)_2$ soln. of the excess of Na oxalate.

G. S. SMITH

2916. Spectrophotometric determination of gallium in rocks and minerals. F. Culkin and J. P. Riley (Dept. of Oceanography, Univ. of Liverpool). *Analyst*, 1958, **83**, 208-212.—Silicate minerals are decomposed by fuming with H_2SO_4 and HF, sulphide minerals by evaporation with Br, HCl and HNO_3 , oxide minerals by fusion with potassium pyrosulphate, and carbonate minerals by solution in dil. HCl. The residue is dissolved in 6.5 N HCl, the soln. is treated with $TiCl_3$, which reduces the reagent blank, and then extracted with diisopropyl ether. The extract is evaporated to dryness and the residue is dissolved in 6.5 N HCl containing $TiCl_3$. The soln. is treated with a chlorobenzene-carbon tetrachloride mixture (3:1, by vol.) and rhodamine B soln. and, after prolonged shaking (10 min.), the organic layer is mixed with ethanol and adjusted to a known vol. with the solvent. The extinction is measured at 562 m μ and referred to a calibration graph. Beer's law is obeyed up to at least 10 μg of Ga.

A. O. JONES

2917. Spectrographic determination of gallium in silicate rocks and minerals. L. A. Borisenok (M.V. Lomonosov Moscow State Univ.). *Zhur. Anal. Khim.*, 1957, **12** (6), 704-707.—In the spectrographic determination of Ga with a d.c. arc (220 V, 15 amp.) between carbon electrodes, the use of NaCl (twice the wt. of the sample material) as a buffer permits the use of a single calibration curve for all types of minerals, lowers the arc temp. and reduces the effect of other elements on the burning of the arc, reduces background intensity and the intensity of the line Fe 2943.57 Å (thus raising the sensitivity for the determination of Ga by means of the line 2943.64 Å ten times), and improves the reproducibility of results by stabilising the arc. As an internal standard Sn is introduced as $SnCl_4$ and the intensity of the Ga line is compared with that of Sn 3034.1 Å.

G. S. SMITH

2918. Fluorimetric determination of thallium with rhodamine B. Hiroshi Onishi (Gov. Ind. Res. Inst., Nagoya, Kita-ku, Japan). *Bull. Chem. Soc. Japan*, 1957, **30** (8), 827-828.—The fluorescence of rhodamine B chlorothallate may be used to determine 1 to 18 μg of Tl. The chemical procedure

for the separation of Tl and extraction of the rhodamine B compound with benzene is the same as for the photometric determination (*Anal. Abstr.*, 1958, **5**, 2141). The fluorescence is measured at 580 m μ . Linear calibration curves are obtained. Rhodamine B fluoresces at 575 m μ , so can be used as a reference standard to adjust the fluorimeter scale. Only Pb, Bi and Sn are extracted with Tl, and these do not interfere. The fluorimetric method appears to have no advantages over the absorptometric method.

A. B. DENSHAM

2919. Differential spectrophotometric determination of rare earths. C. V. Banks, J. L. Spooner and J. W. O'Laughlin (Iowa State Coll., Ames, U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part 1), 458-462.—The optimum conditions for these determinations have to be determined experimentally rather than theoretically. Mixtures such as Nd - Er, Pr - Er and Pr - Nd - Sm can be determined with a coeff. of variation of $\pm 0.17\%$ by a general method and of $\pm 1.25\%$ by a trace-analysis method.

K. A. PROCTOR

2920. Separation of rare earths by means of ethylenediaminetetra-acetic acid. IV. Separation on ion exchangers. G. Brunisholz (Lab. de Chim. Minérale et Anal., Univ. de Lausanne). *Helv. Chim. Acta*, 1957, **40** (6), 2004-2007 (in French).—A single column of resin ($Cu^{2+} + NH_4^+ + H^+$ form) containing adsorbed formic acid (for the yttrium group) or acetic acid (for the cerium group) is used. The rare earths are loaded on the column as 0.1 M soln. of their complex EDTA salts ($M[R-EDTA]$) (M is Na, K or NH_4 , and R is rare earth), and a 0.2 M soln. of $(NH_4)_2Mg-EDTA$ is used as eluent. Pptn. of H_4-EDTA , $H[R-EDTA] \cdot 6H_2O$, or $H_2Mg-EDTA \cdot 6H_2O$ is prevented by buffering the eluent with ammonium formate or acetate. Rare-earth concn. as high as 0.6 equiv. per litre are obtained in the eluate.

M. DAVIS

2921. Paper-electrophoretic separation of rare earths using one per cent. citric acid as electrolyte. M. Lederer (Inst. du Radium, Lab. Curie, Paris). *J. Chromatography*, 1958, **1** (1), 86-89 (in English).—Mobilities are given for several rare earths in paper electrophoresis, in 1% citric acid in a horizontal moist chamber, for 3.5 hr. at 300 V, the current being 6 mA initially, rising to 10 to 11 mA. The fastest moving element was La, the slowest were Lu and Yb. For comparison between one sheet and another, mobilities were calculated to a movement of 100 mm for Lu and Yb, which move with practically the same speed. The observed sequences agree well with those obtained by ion exchange with glycolic acid elution, except that Y moves much faster in the electrophoresis. Few separations were obtained among the yttrium earths.

R. E. ESSERY

2922. Quantitative separation of cerium with potassium iodate. Precipitation from a homogeneous solution. Kenjiro Kimura, Haruo Natsume and Yasuo Suzuki (Chem. Dept., Fac. of Sci., Tokyo Univ., Hongo). *Japan Analyst*, 1957, **6** (11), 719-723.—The method of Willard and Yu (*Anal. Abstr.*, 1954, **1**, 660) for the pptn. of Ce was examined with the aid of ^{144}Ce and ^{146}Sc . The copptn. of Sc decreases and the loss of Ce increases with increase in concn. of HNO_3 , 3 N being the optimum concn. A soln. of rare earths in 3 N HNO_3 (free from Th) is treated with 3% H_2O_2 , cooled, mixed with KIO_3 (≈ 50 times the wt. of the

CeO₂) and KBrO₃ (≈ 15 times) and heated on a water bath for 15 min. The same amount of KBrO₃ is added and the soln. is set aside for 1 hr., then filtered and washed with 5% HNO₃ containing 1 g of KIO₄ per 100 ml. K. SAITO

2923. Determination of metals with a standard solution of potassium ferrocyanide. XI. Determination of cerium. Yoshio Fujita (Dept. of Applied Chem., Fac. of Engng, Osaka Univ., Miyakojima-ku). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (12), 1761-1764.—The precipitation titration of Ce³⁺ (6 to 100 mg per 50 ml) (potentiometrically studied by Shemyakin *et al.*, *Zhur. Obshch. Khim.*, 1937, **7**, 1328) can be carried out with K₄Fe(CN)₆ soln. by the use of iodine (0.1 N, 0.02 ml) - starch (0.2%, 1 ml) soln. as indicator. The optimum conditions are a pH of 4.6 to 6.2 (ammonium buffer); temp., 10° to 25°; rate of titration, 2 to 5 sec. per drop; ethanol content 20 to 30%. Ions that produce insol. salts or undergo redox reaction with I⁻, Ce³⁺ or Fe(CN)₆⁴⁻ cause interference. K. SAITO

2924. Volumetric determination of phosphates and of metals in the presence of phosphates. III. The volumetric determination of lanthanum and neodymium in the presence of phosphates. J. A. R. Genge and J. E. Salmon (Battersea Coll. of Technol., London). *Lab. Practice*, 1957, **6** (12), 695-696.—Lanthanum and neodymium soln. are treated with excess of EDTA (disodium salt) and back-titrated with ZnSO₄ soln. at pH 10, after previous removal of phosphate with (BiO)ClO₄ and titration of the excess of Bi with EDTA at pH 2. *Procedure*—The soln. containing La or Nd and PO₄³⁻ is made acid with HNO₃, and excess of (BiO)ClO₄ soln. ($\approx 0.05 M$) is added. The pptd. phosphate is filtered off after being set aside, preferably overnight, and after being adjusted to pH 2 the filtrate and washings are titrated with $\approx 0.01 M$ EDTA (disodium salt), with catechol violet as indicator (for the Bi end-point). A known vol. of EDTA soln. in excess is then added, the pH is adjusted to 10, and the excess of EDTA is titrated with ZnSO₄ soln., with Eriochrome black T as indicator. The method becomes inaccurate if the molar ratio of PO₄³⁻ to rare-earth metal is greater than 10:1. E. J. H. BIRCH

2925. Influence of copper, nickel and cobalt charging of ion-exchange resin columns on the separation of a praseodymium-neodymium mixture by elution with Trilon A [nitrilotriacetic acid]. G. Weidmann and G. Liebold (Chem. Inst. der Hochschule, Bamberg, Germany). *Angew. Chem.*, 1957, **69** (23), 753.—A method is discussed for the separation of rare-earth metals by the use of ion-exchange resins in their heavy-metal form (Cu, Ni or Co), with nitrilotriacetic acid (sodium salt) soln. as the eluent. The efficiency of the columns increases in the order Cu, Ni, Co. E. G. CUMMINS

2926. The spectrochemistry of actinium. W. F. Meggers (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *Spectrochim. Acta*, 1957, **10** (2), 195-200.—The wavelengths (2558 Å to 7866 Å), the estimated relative intensities in arc, spark and hollow-cathode sources, and the energy levels of 109 strong lines are listed. Thirty-two lines are characteristic of Ac I, 63 of Ac II, 7 of Ac III, 2 possibly of Ac IV and 5 of Ac O. The strongest observed line (2626.44 Å) has intensity 5000 in the spark. K. A. PROCTOR

2927. Detection of the cyanide ion. S. P. Yankov. *Zhur. Anal. Khim.*, 1957, **12** (6), 759.—Finely divided Al₂O₃ (20 parts) and benzidine (1 part) are mixed and placed in a glass tube (6 mm in diameter and 40 mm long) so that a 20-mm column is obtained. A soln. of Cu acetate (0.05 ml), prepared by mixing 100 ml of a N soln. of (CH₃COO)₂Cu.2H₂O and 5 ml of 5 N acetic acid, is introduced and followed by 0.05 ml of the soln. to be tested for CN⁻. A blue zone appears within a few seconds in the presence of $< 0.15 \mu\text{g}$ of CN⁻. Interference is caused by Cl⁻, Br⁻, I⁻ and SCN⁻. In their presence 1 μg of CN⁻ can be detected if the column is moistened with 95% ethanol before the introduction of reagent and test soln. G. S. SMITH

2928. New reagent for the colorimetric micro-determination of hydrocyanic acid. P. Malatesta and M. Dubini (Rome Univ., Italy). *Ric. Sci.*, 1957, **27** (12), 3649-3653.—In the Epstein reaction for the determination of cyanides, the 3-methyl-1-phenylpyrazol-5-one may be advantageously substituted by diethyl acetonedicarboxylate. The reddish-violet colour develops in the cold, may be measured after 8 min., and is stable for 16 min. Beer's law is followed at 525 m μ for 0.8 to 2.2 mg of CN⁻. Ethyl acetoacetate or ethyl benzoylacetate may be substituted over the range 2 to 5 μg of CN⁻, but slight heating is necessary to develop the colour, which is stable for 16 or 20 min. respectively. The diethyl acetonedicarboxylate is the most stable reagent; the pyridine soln. gives satisfactory results after 16 days; cyanide soln. of pH 4 to 7.6 are suitable. The other two compounds give reagents that deteriorate after a few days, but cyanide soln. of pH 4.5 to 9.5 may be used. L. A. O'NEILL

2929. New methods of analysis of silicates. I. A. Voinovitch (Centre Nat. d'Études et Recherches Ceramiques, France). *Chim. Anal.*, 1957, **39** (12), 454-460.—A critical examination is presented of several recent chemical and physical methods of analysis of natural silicates, glasses, ceramics and refractories, with 26 references. It is claimed that a combination of chemical and physical methods of analysis will give greater precision than either alone. R. E. ESSERY

2930. Spectrographic determination of calcium, magnesium, copper, aluminium, iron, titanium and boron in high-purity silicon. R. R. Shvangiradze and T. A. Mozgovaya. *Zhur. Anal. Khim.*, 1957, **12** (6), 708-713.—A method based on the use of a d.c. arc between graphite electrodes, one containing a mixture of the sample and carbon powder (4:1), is used to determine $\approx 10^{-4}$ to $10^{-3} \%$ of Ca, Mg, Cu, Al, Fe and Ti in high-purity silicon for semiconductors. For B, at similar concn., an arc burning in N is used. G. S. SMITH

2931. High-voltage electro-dialysis. I. Separation of impurities from silicic and tungstic acids. V. A. Zarinskii, M. M. Farafonov and V. V. Zateeva (V. I. Vernadskii Inst. of Geochem. and Anal. Chem., Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1957, **12** (6), 677-684.—Apparatus for high-voltage electro-dialysis is described, and the degree of separation of impurities (Fe, Cu, Pb, Cd, Sn, Sb and Bi) from SiO₂ and WO₃ is studied. The finely dispersed material in a suitable soln. is placed in a special chamber with electrodes and ion-permeable membranes. Complete separation of

0.001 to 0.01% of Fe, Cu, Pb and Cd from SiO_2 and of Pb and Cd from WO_3 is attainable.

G. S. SMITH

2932. Determination of a trace amount of phosphorus in germanium oxide. Yoshihiro Ishihara and Yasuro Taguchi (Mitsubishi Mining and Metallurgical Lab., Oomiya, Saitama Prefecture). *Japan Analyst*, 1957, **6** (11), 724-727.—The extraction of molybdophosphate with a mixture of butanol and CHCl_3 , followed by colorimetry, with SnCl_2 as reducing agent, was examined for the determination of P ($\approx 0.00001\%$) in germanium dioxide, with reference to the elimination of interference from other elements. Arsenic and Ge are evaporated off in the presence of HBr and HCl; Si is converted into SiO_2 by heating with HClO_4 ; and the addition of NaBF_4 decomposes any zirconium or tungsten complex with P. Vanadium is pptd. with 8-hydroxyquinoline (I) and extracted with CHCl_3 . *Procedure*—Heat the sample (5 g) with 6 N HCl (80 ml) and HNO_3 (1 ml) with occasional addition of H_2O_2 (30%, total 5 ml). Heat the resulting soln. with HClO_4 (2 ml) until white fumes are evolved. Repeat the heating with HCl (1 + 1, 5 ml) and HBr (3 ml), reduce the vol. to 0.5 ml, add water (10 ml), NaBF_4 (5 g of NaF and 30 g of H_2BO_3 in 500 ml of water) (1 ml) and M Na acetate (1 ml). Adjust the pH with aq. NH_3 soln. to 4.5, add I (100 ml of 1.5% soln. in N acetic acid is mixed with 50 ml of M Na acetate) (3 ml) and extract with CHCl_3 (10 ml). Add water (2.5 ml), 8 N HNO_3 (2.5 ml) and ammonium molybdate (10%, 2 ml) and shake with butanol- CHCl_3 (1 + 3, by vol). Shake the org. layer with SnCl_2 (1% in 0.5 N HCl) (5 ml) and measure the extinction at 710 μ .

K. SAITO

2933. Use of naphthalene derivatives in inorganic analysis. IV. The nitronaphthylamines as fluorimetric reagents for stannous tin. J. L. Garnett and L. C. Lock (School of Appl. Chem., N.S.W. Univ. of Technol., Sydney, Australia). *Anal. Chim. Acta*, 1957, **17** (6), 574-578 (in English).—Thirteen of the 14 possible nitronaphthylamines gave an intense blue fluorescence with Sn^{2+} when 0.02 ml of a 0.1 M soln. of Sn^{2+} was placed on Whatman 3MM chromatographic paper, air-dried for 30 min., sprayed with reagent (1% nitronaphthylamine in absolute ethanol-10 N HCl, 1:1), air-dried, and examined under u.v. light. The paper was then sprayed with 15 N aq. NH_3 , dried, and again examined under u.v. light for quenching. The presence of HCl in the reagent is necessary for maximum sensitivity. Of 47 ions examined, 23 gave fluorescence before quenching, but only Sn^{2+} gave fluorescence with all reagents after quenching. When tested for sensitivity in the presence of H_2PO_4 (Anderson and Garnett, *Ibid.*, 1957, **17**, 452), all reagents would detect $\approx 10^{-7}$ g of Sn^{2+} , but 5- and 6-nitro-2-naphthylamines gave the most intense fluorescence. It is suggested that all nitronaphthylaminesulphonic acids will give a fluorimetric test with Sn^{2+} , their advantage over the nitronaphthylamines being that they can be applied in aq. soln.

R. E. ESSERY

2934. Polarographic determination of small amounts of tin. S. Kallmann, R. Liu and H. Oberthün (Res. Div., Ledoux & Co., 359, Alfred Avenue, Teaneck, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 485-487.—The rapid method described can be used for the determination of 0.2 to 50 mg of Sn in complex materials. The Sn is separated by steam-distillation with HBr in a

modified Kjeldahl apparatus, and the subsequent polarography is carried out in a bromide-chloride medium. Arsenic does not interfere with the determination, but Sb has a slight repressing effect.

K. A. PROCTOR

2935. New method of determining sulphide tin in ores. L. V. Zverev and N. V. Petrova (All-Union Inst. of Mineral Raw Materials). *Zavod. Lab.*, 1957, **23** (12), 1403-1405.—Sulphide, but not oxide, ores of tin react with Cl or Br in CCl_4 in the presence of elementary S to give SnCl_4 or SnBr_4 , which dissolves in the CCl_4 . The sample (0.5 to 2 g) in a dry flask is treated with 25 ml of CCl_4 , 10 ml of Br and 1 g of S. The liquid without being heated is stirred for 2.5 hr. and filtered, the residue being washed with CCl_4 . The Sn corresponding to sulphide tin in the ore is extracted from the filtrate by shaking with an equal vol. of dil. H_2SO_4 (1:1) and is determined iodimetrically. The matter insoluble in CCl_4 contains the oxide tin, and in it can be determined acid-soluble SnO_2 and cassiterite.

G. S. SMITH

2936. Analysis of mixtures of tin, stannous and stannic oxides. F. Gauzzi (Ist. Metallurg. Metallogr., Univ., Rome). *Ann. Chim., Roma*, 1957, **47** (12), 1316-1320.—The tin in a Sn-SnO (I)- SnO_2 (II) mixture is extracted by treating the mixture with 5% $\text{Fe}_2(\text{SO}_4)_3$ soln. under CO_2 , the residue (I, II) is filtered off and Fe^{2+} are determined by titration with KMnO_4 in the presence of H_3PO_4 . The I is then extracted with 4% oxalic acid-4% ammonium oxalate and the Sn is recovered by electrolysis of the soln. in the presence of hydrazine sulphate. Finally the residue (i.e., II) is heated at 950° to 1100° and weighed.

A. G. COOPER

2937. Polarographic determination of tin in zirconium alloys. J. H. Porter, II (Res. and Development Div., Corning Glass Works, Corning, N.Y., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 484-485.—Tin in zirconium alloys in the range 0.06 to 1.95% can be determined polarographically without any separations. The sample is dissolved with a mixture of sulphuric, hydrochloric and fluoroboric acids under a stream of nitrogen. For 12 samples of alloys containing 0.25% or 0.5% of Sn the standard deviation was 0.008%.

K. A. PROCTOR

2938. [Polarographic] determination of small amounts of lead in pure metals and ferrous alloys. L. S. Nadezhina and V. P. Razumova (M. I. Kalinin Leningrad Polytech. Inst.). *Zhur. Anal. Khim.*, 1957, **12** (6), 731-735.—The method is based on co-pptn. of PbSO_4 with SrSO_4 , dissolution of the ppt. in alkaline EDTA (disodium salt) soln., neutralisation and polarographic determination of Pb. The conditions affecting the determination of Pb in the presence of EDTA are studied. In acid medium (pH > 4.8) EDTA does not form a complex with Pb and E_1 is ≈ -0.40 V. At pH 6.5 the reduction potential becomes more negative ($E_1 = -1.3$ V) and the wave height is halved. At higher pH values, E_1 remains approximately the same, but the wave height increases with pH and reaches the original value at pH 11. The optimum conditions for determining Pb with the dropping mercury electrode are pH 3.5 and EDTA (disodium salt) concn. 0.1%; the wave height is directly proportional to the concn. of Pb. The method of addition can be used. To determine Pb (0.002 to 0.01%) in steel the sample (5 to 10 g) is dissolved in dil. H_2SO_4 (1:4) (20 ml per 1 g),

boiling water (20 to 25 ml) is added and the soln. is boiled for a few minutes. After oxidation with HNO_3 the soln. is evaporated to fuming, then diluted to ≈ 200 ml and, if W and Mo do not exceed 1%, it is treated with 10 ml of 1% $\text{Sr}(\text{NO}_3)_2$ in small portions and set aside for 2 to 3 hr. The soln. is filtered without transfer of the ppt., which is washed with 1% H_2SO_4 soln. and then once with hot water. The ppt. is then dissolved in a small amount of a 3% soln. of EDTA (disodium salt) in 2 N NaOH. After neutralisation with HCl to methyl orange indicator the soln. is diluted to 25 ml and the Pb is determined polarographically in 10 ml after passage of CO_2 to remove O. In the presence of Mo, W and V in large amounts, the diluted soln. obtained after the fuming is treated with excess of Na_2CO_3 to precipitate Pb with Ni, Fe, Cr and Mn, leaving Mo, W and V in soln. The ppt. is dissolved in dil. H_2SO_4 and Pb is co-pptd. with SrSO_4 , as described above.

G. S. SMITH

2939. Determination of lead sulphate in the active masses of lead accumulators. V. V. Ten'kovtsev, E. N. Rozenblyum, Z. S. Kryukova and F. M. Klebanova (Sci. Res. Accumulator Inst., Leningrad). *Zhur. Anal. Khim.*, 1957, **12** (6), 736-739.—Boiling with Na_2CO_3 soln. is an unsatisfactory method of decomposing PbSO_4 in the presence of the PbO_2 , which hinders the diffusion of the reagent into the interior. A suitable method of determining PbSO_4 is described. The finely divided sample (3 g) is treated with 15 ml of dil. HCl (1:1) if the positive mass is to be analysed, or 15 ml of a mixture of equal vol. of 5 N acetic acid and 5 N ammonium acetate for the negative mass. After being boiled with continuous stirring for 2 to 3 min., the soln. is mixed with 25 ml of water and treated with 1 to 2 g of zinc filings, and then boiled until the Pb is completely deposited. After removal of the Pb and Zn, the SO_4^{2-} are determined by any standard method.

G. S. SMITH

2940. Spectrophotometric determination of titanium with hydrogen peroxide and ethylenediamine-tetra-acetic acid. Soichiro Musha and Kinya Ogawa (Fac. of Engng, Osaka Prefectural Univ., Sakai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (11), 1686-1690.—Complex formation between Ti^{4+} and EDTA was studied in the presence of H_2O_2 under various conditions. The complex appears to have an empirical formula $[\text{TiO}(\text{H}_2\text{O}_2)\text{Y}]^{2-}$ (Y is the EDTA radical) and the absorption spectrum (max. 365 $\text{m}\mu$) remains unchanged at pH 0.4 to 4. In a more basic soln., the intensity of the colour gradually decreases. The extinction coeff. at 365 $\text{m}\mu$ is proportional to the amount of Ti (4 to 40 p.p.m.) in 0.05 N H_2SO_4 in the presence of a small excess of EDTA. No interference results from <200 p.p.m. of Al, Zn, Zr, alkaline-earth and alkali metals, whilst coloured ions, Mo and V vitiate the estimation. Titanium (0.3 to 3 mg) can also be titrated photometrically (450 $\text{m}\mu$) with 0.05 N EDTA in 0.05 N H_2SO_4 in the presence of a few drops of H_2O_2 (30%).

K. SAITO

2941. Rapid determination of hydrogen in titanium and its alloys. Nakaaki Oda and Katsusuke Norishima (Takaoka Plant, Nippon Soda Co., Ltd., Takaoka, Toyama Prefecture). *J. Electrochem. Soc. Japan*, 1957, **25** (5), 269-273.—A combustion method was examined with the apparatus normally used for steel analysis. Hydrogen (0.003 to 0.5%) in titanium (10 to 50 mesh) is quant. converted into water at 1250° within 10 min. in a current of

O (180 ml per min.). Finer samples are mixed with the same amount of Sn and heated at 1300° to 1350° for 10 min. Samples of 4 g for <0.1% of H and 1 g for >0.1% of H are used. The results agree well with those obtained by the vacuum-fusion method for >0.005% of H.

K. SAITO

2942. Quantitative determination of carbon in titanium and its alloys. Nakaaki Oda and Katsusuke Norishima (Takaoka Plant, Nippon Soda Co., Ltd., Toyama Prefecture). *J. Electrochem. Soc. Japan*, 1957, **25** (6), 319-322.—The use of the apparatus normally employed for the determination of C in iron was examined. To avoid the influence of a small amount of Cl, the use of silver gauze (30 to 40 mesh) (heated at 400°) in the combustion tube is advisable. A rapid combustion (1400° to 1450°, 10 min.) of titanium (4 g for <0.5% of C, 1 g for >0.5%; covered with 30 to 40-mesh tin) in a current of O (≈ 200 ml per min.) often results in mechanical damage of the boat; the use of a "double boat" (porcelain) is recommended. The relative error is <7% and the time taken for a determination is ≈ 20 min.

K. SAITO

2943. Simultaneous quantitative determination of carbon and hydrogen in titanium and its alloys. Nakaaki Oda and Katsusuke Norishima (Takaoka Plant, Nippon Soda Co., Ltd., Takaoka, Toyama Prefecture). *J. Electrochem. Soc. Japan*, 1957, **25** (7), 365-368.—By the combination of the methods reported previously (cf. *Anal. Abstr.*, 1958, **5**, 2941, 2942), a rapid (<25 min.) simultaneous determination of C and H can be carried out, the error being almost the same as in the individual analyses. The use of heated (400°) silver gauze (30 to 40 mesh) for the elimination of the influence of Cl does not vitiate the determination of H.

K. SAITO

2944. Determination of nitrogen in titanium and its alloys. Nakaaki Oda and Shigeji Sawabe (Takaoka Plant, Nippon Soda Co., Ltd., Toyama Prefecture). *J. Electrochem. Soc. Japan*, 1957, **25** (12), 620-625.—The rapid (<50 min.) determination of N (>0.001%) in titanium metal was studied by the Kjeldahl method. The sample (5 g) is best dissolved with HCl (1 + 1, 80 ml) and HF (46%, 4 ml). The HCl soln. is treated with NaOH soln. (50%, 100 ml) and the NH_3 is distilled (≈ 120 ml) into 0.01 N HCl (20 ml). Insol. titanium nitride is filtered off after distillation and fused with $\text{K}_2\text{S}_2\text{O}_7$ (10 g) and H_2SO_4 (10 ml); the presence of Se (0.5 g) decreases the time for dissolution. The melt is treated with NaOH and the NH_3 is distilled similarly. The average error is <6%.

K. SAITO

2945. Conductimetric determination of small amounts of oxygen in titanium. M. Codell and G. Norwitz (Frankford Arsenal, Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 524-526.—In the improved bromination-absorption apparatus and procedure described, the sample (0.2 g), prepared as described previously (*Ibid.*, 1956, **28**, 2006), is treated at $\approx 925^\circ$ with Br and graphite in an atm. of argon. The CO produced is oxidised on hot CuO to CO_2 , which is then absorbed in aq. $\text{Ba}(\text{OH})_2$ soln. and the change in conductivity is measured. Less than 0.05% of O can be determined in ≈ 75 min. with an accuracy equiv. to that of the gravimetric method and a standard deviation of $\approx 0.015\%$ (on 6 analyses). The method is unsatisfactory for steel.

W. J. BAKER

2946. Determination of oxygen and hydrogen in titanium. Z. M. Turovtseva and R. Sh. Khalitov (V. I. Vernadskii Inst. of Geochem. and Anal. Chem., Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1957, **12** (6), 720-722.—The sample is mixed with coarse graphite powder (10 to 20 mesh) and vacuum extraction is carried out in two stages (i) at 1000° for 5 min. and (ii) at 1850° for 30 min. Only H appears in the first stage. The second stage yields CO with small amounts of H. The combined gases are analysed. The crucible containing the sample is then heated to 2100° in preparation for the introduction of another sample. Fine graphite powder is unsuitable since a carbide film forms over the powder and interferes with further reaction.

G. S. SMITH

2947. Determination of zirconium by amperometric titration with cupferron. Yu. I. Usatenko and G. E. Bekleshova (F. Z. Dzerzhinskii Dnepropetrovsk Chem.-Tech. Inst.). *Zavod. Lab.*, 1957, **23** (12), 1406-1407.—The chloride or sulphate soln. containing >6 mg of ZrO_2 is made 2 to 3 N in H_2SO_4 . After addition of 3 g of NaCl the soln. (30 to 35 ml) is titrated amperometrically at room temp. at 0.8 V vs. the S.C.E. on a rotating platinum electrode (900 r.p.m.) with a soln. of cupferron. No interference is caused by Al, Cr, Mn, Zn, Ni and F, nor by Cu if it does not exceed twice the amount of Zr. In 2 to 3 N acid, Fe^{3+} are not titrated by cupferron but they are partially pptd. with Zr. Interference is caused by Ti, V^{5+} , oxidising agents capable of oxidising cupferron and reducing agents giving an anodic diffusion current at 0.8 V. To determine ZrO_2 (67%) in silicates, the sample (0.1 g) is fused with 20 times its wt. of Na_2CO_3 , the melt is extracted with dil. HCl (1:3) and an aliquot is taken.

G. S. SMITH

2948. Colorimetric determination of zirconium with phenylfluorone. F. G. Zharovskii and A. T. Pilipenko (T. G. Shevchenko Kiev State Univ.). *Zavod. Lab.*, 1957, **23** (12), 1407-1410.—With Zr, phenylfluorone (I) gives a red ppt. or a red coloration due to the presence of $Zr(C_6H_5O_2)_4$. The optimum acidity (HCl) is 0.4 to 0.5 N, but complete development of the colour is attained within 20 min. with 0.6 to 0.7 N HCl. In the presence of gelatin the colour is stable for >4 hr. The max. absorption is at 535 $m\mu$ where the reagent itself shows practically no absorption. The minimum amount detectable in HCl or HNO_3 soln. is 0.32 μg per ml, and in H_2SO_4 soln. is 2.4 μg per ml. The sensitivity can be raised by shaking the soln. with 1 or 2 ml of CCl_4 and examining the interface for a red film. The minimum amount detectable is then 0.12 μg in HCl soln. and 0.8 μg in H_2SO_4 soln. The compound of I with Zr is soluble in ethanol, isomyl alcohol, butanol, butyl formate, ethyl methyl ketone and cyclohexanone, but the red colour is stable for a long time only in alcoholic soln. Alkali metals, alkaline earths, Th, Al, Zn, Cd and other bivalent metals do not react with I. Interference is caused by coloured ions and also by Ti, Sn, Sb, Ta, Nb, Hf, H_3PO_4 and HF. Contents of Fe^{3+} , Cr^{3+} , Ti^{4+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Bi^{3+} , Ag^+ , V^{5+} , Mo^{6+} and W^{6+} greater than 50, 200, 3, 200, 500, 200, 50, 300, 100, 1 and 5 times, respectively, that of the Zr cause interference. To determine Zr in alloys of Mg and Al, the sample (0.05 to 0.5 g) containing 0.01 to 0.5 mg of Zr is dissolved in 10 ml of dil. HCl (1:1), first by treatment in the cold and then by heating, with the subsequent addition of 1 ml of HNO_3 if the soln. is cloudy, followed by removal of oxides of N. The

soln. is diluted to 50 ml with water, and two aliquots (5 or 10 ml) are taken. The acidity of one is determined by titration with 0.1 N NaOH in the presence of methyl orange and the result is used to adjust the acidity of the other aliquot [after dilution to 25 ml] to 0.5 N. After addition of 1 ml of 0.5% gelatin soln. and 5 ml of a 0.03% soln. of I in ethanol, the soln. is diluted to 25 ml, and the extinction is measured at 535 $m\mu$ after 20 min.

G. S. SMITH

2949. Differential spectrophotometric determination of zirconium in presence of hafnium. H. Freund and W. F. Holbrook (U.S. Dept. of the Interior, Bureau of Mines, Albany, Oreg., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 462-465.—By applying the alizarin red differential method of Manning and White (*Anal. Chem.*, 1951, **23**, 580) it is possible to obtain results that are comparable in accuracy and precision with those obtained by gravimetric techniques.

K. A. PROCTOR

2950. Dissolution of metallic zirconium in sulphuric acid and ammonium sulphate. Takashi Amako and Kouzi Onoue (Developing Dept., Osaka Titanium Co., Higashihama, Amagasaki). *Japan Analyst.*, 1957, **6** (11), 735-736.—The dissolution of zirconium sponge (10 to 16 mesh) in H_2SO_4 is more rapid (≈ 30 min.) in the presence of $(NH_4)_2SO_4$ [for 5 g of Zr, 30 ml of H_2SO_4 and 20 g of $(NH_4)_2SO_4$]. Without the use of HF, the determination of Fe, Mn, Mg and Ti is simplified. Silicon remains undissolved.

K. SAITO

2951. The determination of nitrogen in silicon nitride. M. Billy and J. Lamure. *Compt. Rend.*, 1957, **245** (25), 2289-2290.—The procedure is to heat the sample (0.1 g) for ≈ 3 hr. in *vacuo* at 1000° with a 15 to 20-fold excess of a mixture (1 + 1) of $PbCrO_4$ and PbO . Oxygen is removed by including a column of reduced copper heated to 550° in the apparatus. Accuracy is high for iron and steel alloys. Oxidation with Na_2O_2 in *vacuo* at 400° is not so satisfactory because of the large vol. of O evolved. The standard Kjeldahl method gives low results because Si_3N_4 is not completely decomposed by conc. H_2SO_4 .

W. J. BAKER

2952. Continuous determination of nitric oxide concentration in coke gas. M. T. Borok (State Design Bureau for Anal. Apparatus Construction). *Zavod. Lab.*, 1957, **23** (12), 1420-1424.—The method is based on the oxidation of NO to NO_2 by means of ozone generated in a simple apparatus (e.g., that of Dudden, *Gas World*, 1945, **122**, 276) and absorption in aq. *m*-phenylenediamine soln., with automatic photometric determination of the extinction.

G. S. SMITH

2953. A new method for the micro-determination of arsenic by the application of internal electrolysis. (Studies on metallic reducing agents in analytical chemistry.) Chozo Yoshimura (Fac. of Sci. and Engng, Kinki Univ., Fuse, Osaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (11), 1586-1588.—Arsenite (0.0005 to 1 mg) is reduced to AsH_3 by internal electrolysis with zinc amalgam as anode (cathode, platinum plate; anodic soln., 6 N H_2SO_4 ; cathodic soln., the sample in dil. H_2SO_4 ; diaphragm, porous porcelain plate). The evolved gas is detected by the Gutzeit method. The amount of AsH_3 liberated is not quant., but reproducible enough to

be determined by this method, provided that the calibration curve is prepared under the same conditions.

K. SAITO

2954. Analysis of pure metals. Determination of arsenic as impurity. V. A. Nazarenko, G. V. Flyantikova and N. V. Lebedeva. *Zavod. Lab.*, 1957, **23** (8), 891-896.—Methods based on the volatilisation of AsH_3 and on the extraction of diethyldithiocarbamate from acid soln. by CHCl_3 , followed in either case by the colorimetric determination of As as the arsenomolybdenum-blue complex, are described. By extraction of the blue complex with isoamyl alcohol, 0.1 μg of As in 10 ml of soln. can be determined. High-purity reagents are required; their preparation is described. The arsine method is used for the determination of As in antimony, niobium, vanadium and silicon, and the diethyldithiocarbamate method for the determination of As in gallium, indium and thallium.

Determination in antimony.—The sample (1 g, or if the content is $>0.0005\%$, 0.2 to 0.5 g) is decomposed with 5 ml of conc. HNO_3 to give a white mass, 6 g (or 5 g with 0.5 g sample wt.) of ammonium hydrogen tartrate, followed by 80 ml of water, is added, and the mixture is heated to give a clear soln. Then the soln. is diluted to 150 ml and cooled, and treated with 10 ml of 1-92% KH_2PO_4 soln. (100 mg of P_2O_5) and 10 ml of magnesia mixture specially purified (Lockemann, *Z. anal. Chem.*, 1923, **62**, 353), followed by aq. NH_3 until a ppt. starts to form. Excess of aq. NH_3 (7.5 ml) is added and the ppt. is filtered off after 12 to 16 hr. and washed with 1% aq. NH_3 . The ppt. is then dissolved in hot dil. H_2SO_4 (1:10) (≈ 50 ml) and the soln. is mixed in a distillation flask with 2 ml of 15% KI soln. and 0.5 ml of SnCl_2 soln. (concen. not stated) and set aside for 30 min. After addition of 5 g of granulated zinc to the cold soln., the AsH_3 is distilled into a centrifuge tube containing 1 ml of 1.5% HgCl_2 soln., 0.20 ml of 6 N H_2SO_4 and 0.20 ml of 0.1 N KMnO_4 . Passage of H through the absorbing soln. lasts for 1.5 hr. Meanwhile amounts of a standard soln. of As containing from 0 to 5 μg with 0.5- μg intervals are placed in a series of tubes, the soln. are diluted to 2 ml, to each is added HgCl_2 , etc., as described above, and the soln. are heated for 5 min. and set aside to cool. The sample and standards are mixed with 5 ml of molybdate-hydrazine reagent (10 ml of a soln. of 0.25 g of hydrazine sulphate in 100 ml of water is mixed, as required, with 10 ml of a soln. of 1 g of ammonium molybdate in 10 ml of water, treated with 90 ml of 6 N H_2SO_4 , and the mixture is diluted with 80 ml of water), immersed in boiling water for 15 min., then cooled and shaken with isoamyl alcohol (10 \times 1 ml). A blank (with the amount of KMnO_4 reduced to 0.15 ml) is carried out at the same time. The colours of the alcohol layers are compared.

Determination in niobium.—The sample (1 g) is dissolved (10 to 15 min.) in 4 g of $\text{K}_2\text{S}_2\text{O}_8$ and 10 ml of conc. H_2SO_4 in a Kjeldahl flask. The soln. is mixed gradually with a mixture of 100 ml of 7% ammonium hydrogen tartrate soln. and 2 ml of 30% H_2O_2 to give a yellow opalescent soln., which is then cooled and treated with KH_2PO_4 soln., magnesia mixture, etc., as described above.

Determination in vanadium.—The sample (1 g) is dissolved in 10 ml of conc. HNO_3 and the soln. is heated with 10 ml of conc. H_2SO_4 to remove oxides of nitrogen. The cooled soln. is mixed with 10 g of oxalic acid and evaporated carefully to fuming. After the addition of 100 ml of water, the soln. is cooled, treated with 1 ml of SnCl_2 soln. and 0.2 ml of 15% KI soln.,

and set aside for 30 min. Granulated zinc (7 g) is added to the soln. in a flask and the AsH_3 is distilled off as described above under antimony.

Determination in silicon.—The sample (1 g) is dissolved in NaOH soln., the soln. in a distillation flask is treated with 30 ml of water, 15 ml of conc. HCl, 2 ml of 15% KI soln. and 0.5 ml of SnCl_2 soln., then set aside for 15 min., after which 5 g of zinc is added and the AsH_3 is distilled off.

Determination in gallium and indium.—The sample (0.4 g) is dissolved in 2 ml of water, 3 ml of conc. H_2SO_4 and 2 ml of conc. HNO_3 . The soln. is evaporated three times with the addition of 5-ml amounts of water until salts deposit. Finally 5 ml of water and 0.25 ml of sodium metabisulphite soln. are added and the soln. is boiled, with the addition of water as necessary, until SO_2 is removed. The soln. diluted to 40 ml at 40° to 45° is treated with 1.5 ml of 20% KI soln. and 1 ml of freshly prepared 5% ascorbic acid soln., and set aside for 15 min. Then the soln. is shaken twice with 5-ml amounts of a soln. of diethyldithiocarbamic acid in CHCl_3 , prepared by mixing 20 ml of 1% Na diethyldithiocarbamate soln. and 0.8 ml of 6 N HCl at 5° to 10°, extracting with 20 ml of CHCl_3 at 5° to 10°, and keeping the CHCl_3 soln. at not above 10° for 1 hr. The combined extracts are washed twice with 2.5-ml amounts of N H_2SO_4 , evaporated to remove CHCl_3 , and then evaporated to dryness with 1.5 ml of conc. HNO_3 . The residue is treated with 2 ml of 7% $\text{Mg}(\text{NO}_3)_2$ soln. and evaporated to a paste, 0.5 ml of HNO_3 is added and the soln. is evaporated to dryness and then ignited at 500°. The residue is dissolved in 0.2 ml of 6 N H_2SO_4 and the molybdate-hydrazine method is applied.

Determination in thallium.—The sample (0.4 g) is dissolved in 1.5 ml of conc. HNO_3 , 1.2 ml of conc. H_2SO_4 and 5 ml of water are added, the soln. is evaporated to fuming, 5 ml of water is added and the fuming repeated four times. After addition of water and sodium metabisulphite the determination is completed as described under gallium and indium.

G. S. SMITH

2955. Determination of micro amounts of impurities in antimony by the neutron activation method. A. I. Kulak (D. I. Mendeleev Moscow Chem.-Tech. Inst.). *Zhur. Anal. Khim.*, 1957, **12** (6), 727-730.—A method for the determination of very low concn. (10^{-6} to $10^{-7}\%$) of Cu, As, Te, Ni and Co in antimony is described.

G. S. SMITH

2956. Amperometric titration of bismuth with potassium iodide in the presence of amidopyrine. A. K. Zhdanov, V. A. Khadeev and V. Kh. Khalilova (V. I. Lenin Central Asia Univ., Tashkent). *Zhur. Anal. Khim.*, 1957, **12** (6), 695-698.—In 2.5 M H_2SO_4 , containing 500 mg of amidopyrine in 30 ml, Bi is titrated amperometrically with the dropping mercury electrode at 0.5 V applied e.m.f. with 0.35 M KI, which gives a ppt. of an amidopyrine complex with HBiI_4 . No interference is caused by the following ions unless their concn. ratio to that of Bi exceeds the figure shown— NO_3^- 60, Cl^- 50, acetate 100, PO_4^{3-} 45, Fe, Mn, Ni, Co, Zn, Cr, Al and Mn, at least 100, Cd 2.5. Interference is caused by Pb, but if its concn. is not greater than that of Bi it can be pptd. as PbS , which need not be removed before the titration. With higher concn. of Pb some loss of Bi occurs in the pptn. of PbS . The anodic wave due to iodide can also be used in the amperometric titration. The applied voltage is then 0.08 V and gelatin is added. To determine Bi and Cd when present together, the soln., which can contain Cl^- and NO_3^- , is made 2.5 N in H_2SO_4 .

and Bi is titrated as described above. From another portion Bi is removed by pptn. with aq. NH_3 , and Cd is titrated at 1 V as previously described (*Anal. Abstr.*, 1957, 4, 1771).

G. S. SMITH

2957. Determination of bismuth in lead and tin by extractive separation with thionalide. H. Lilie (Dtsch. Amt für Material- und Warenprüfung, Berlin). *Z. anal. Chem.*, 1958, **159** (3), 196-201.—Photometric methods are described for the determination of small amounts of Bi in lead or tin. The results agree within 1% with those obtained polarographically or gravimetrically. The time taken for a determination in duplicate is 75 min. *Procedure for samples of lead*—Dissolve the sample (4 g) in conc. HNO_3 (40 ml), add H_2O (100 ml), cool, add urea (2 g) and shake gently until the evolution of gases has slackened. Dilute to 200 ml, mix and filter. If the concn. of Bi is $>0.1\%$, dilute 10-fold with dil. HNO_3 . Add aq. NH_3 to a 50-ml aliquot to give a pH of 1, cool and extract with a 0.1% soln. of thionalide in CHCl_3 (10 + 5 ml). Wash the combined CHCl_3 layers with H_2SO_4 (10 ml) and extract with H_2SO_4 (1:3) (10 + 5 + 5 ml). Add 5% Na_2SO_3 soln. (10 ml) to the combined extracts, mix with 1-7% KI soln. (8 ml), dilute to 50 ml, filter and measure the yellow colour in a photometer with a S.43 filter. *Procedure for samples of tin*—Dissolve the sample (10 g) in aqua regia and remove most of the excess of acid by evaporation. Cool, and add ammonium tartrate soln. (200 ml of a mixture of 100 g of tartaric acid, 330 ml of H_2O and 170 ml of 25% aq. NH_3). Slowly add 2% Na_2S soln. with constant stirring until pptn. is complete, heat to boiling and filter. Dissolve the ppt. in HNO_3 (1:1) (20 ml) and dilute to 100 ml. Add aq. NH_3 to a 10-ml aliquot to give a pH of 1, cool, and extract with thionalide soln. Complete the determination as described above.

A. R. ROGERS

2958. Analytical solvent extraction of vanadium using acetylacetone. J. P. McKaveney and H. Freiser (Dept. Chem., Univ., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 526-529.—Data on the extraction of VIII, IV and VV into a mixture (1 + 1, by vol.) of acetylacetone and CHCl_3 are given. One extraction of VIII is approx. quant. (93%) at pH 2, and the V can then be determined spectrophotometrically as peroxide at 460 $\text{m}\mu$ with H_2O_2 as a reference solvent. The procedure given is very suitable for steel containing amounts of V too small to be titrated potentiometrically. Reduction of V in the sample soln. is effected with Zn in an atm. of N (30 min. reflux); Fe^{2+} do not affect the extraction, but interference by Ti during the colorimetric procedure should be eliminated by addition of NH_4F . The error is within $\approx 3\%$ for concn. of V from 0.05 to 4%.

W. J. BAKER

2959. Indirect colorimetric determination of vanadium with phenylthiosemicarbazide. Sumio Komatsu and Naohumi Kumagai (Fac. of Liberal Arts, Toyama Univ., Toyama). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (11), 1558-1561.—Phenylthiosemicarbazide (I) is oxidised by the vanadate ion in $>1.5\text{N}$ acetic acid. The resulting soln. has a max. absorption at 420 $\text{m}\mu$ and the extinction is proportional to the concn. of V, in the presence of I in molar concn. greater than that of V. The working curve is linear for $<22.5\text{ }\mu\text{g}$ of V per ml. The colour reaches a maximum 10 min.

after the addition of the reagent and remains unchanged for 20 min. No interference results from Al, PO_4^{3-} , AsO_4^{3-} , Mn ($<700\text{ }\mu\text{g}$ per ml) and Cr ($<90\text{ }\mu\text{g}$). Chromate and permanganate are reduced with SO_3^{2-} ; any simultaneously reduced V is re-oxidised with KMnO_4 , the excess of which is decomposed with oxalic acid. Copper reacts similarly with I, but is removed with Amberlite IR-120 at pH >5 ; Mo ($<32\text{ }\mu\text{g}$ per ml) reacts only slowly and does not cause interference; Fe ($<80\text{ }\mu\text{g}$) is masked with NaF; Hg, Ag, Au, Pt and Pd are reduced with zinc amalgam in 3.5 N acetic acid soln.

K. SAITO

2960. Determination of vanadium by the spectrophotometric method in non-aqueous solution. D. Cozzi and G. Raspi (Ist. di Chim. Anal., Univ. degli Studi, Firenze, Italy). *Anal. Chim. Acta*, 1957, **17** (6), 590-596 (in French).—If a small vol. of soln. of V containing H_2O_2 and HCl is mixed with anhydrous dioxan containing gaseous HCl, an intense red-yellow colour is given by 5 μg of V per ml, which, on addition of salicylaldehyde changes to a violet-blue, with maximum absorption at 565 $\text{m}\mu$, visible with as little as 1 μg of V per ml. For quant. measurement, the soln. containing the V is evaporated to dryness at 100° , the residue is dissolved in 0.2 ml of N HCl in 2% aq. H_2O_2 , and then treated with 5 ml of a reagent composed of 40% acetic anhydride (N in gaseous HCl), 40% glacial acetic acid and 20% methyl salicylate. The extinction is read at 565 $\text{m}\mu$, and referred to a standard curve. Ferric iron does not interfere at a level 2000 times that of the V; Cu, Ni, Cd, U and Cr do not interfere up to 10 times, above that they yield precipitates, which may be centrifuged off and the supernatant liquid read. If much Al is present (>100 times), the reagent should not contain HCl; Co, Mo and W must be absent, as they yield colours absorbing significantly at 565 $\text{m}\mu$.

R. E. ESSERY

2961. Determination of tantalum in niobium. M. L. Theodore (Westinghouse Electric Corp., East Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 465-467.—The sample (2 g) is dissolved in a mixture of acids (HF, followed by the dropwise addition of HNO_3) and, after adjustment of the soln. to 2.2 N HF and N HCl, the Ta is extracted with isobutyl methyl ketone, followed by its pptn. therein with aq. NH_3 . To ensure negligible co-extraction of Nb, the acid soln. of the hydroxide ppt. is adjusted to 0.9 N HF and 2.9 N HCl, and a second extraction and pptn. of Ta is made. The ammoniacal layer is evaporated to dryness, the residue is fused with KHSO_4 and the melt is dissolved in hot 15% tartaric acid soln., which is then filtered and the filtrate made up to 250 ml. The Ta in a 25-ml aliquot is then determined spectrophotometrically at 355 $\text{m}\mu$ in 5-cm silica cells, against the reagent blank, by the pyrogallol method (*cf. Anal. Abstr.*, 1955, 2, 2083). Beer's law is valid up to 1 mg of Ta per 100 ml, and the concn. of Nb should be >0.75 mg. The colour takes ≈ 30 min. to develop. The error is $\pm 1.8\%$.

W. J. BAKER

2962. The paper chromatography of protactinium. J. Vernois (Inst. du Radium, Paris). *J. Chromatography*, 1958, **1** (1), 52-61 (in French).—The separation of Pa from the elements usually accompanying it in natural products (Fe, Hf, Zr, U, Ta, Nb, Bi and Ti), is discussed. The material is dissolved in 1% HF, and separation carried out by ascending chromatography on Whatman No. 1

paper (22 cm \times 22 cm), rolled into a cylinder, for 12 hr. with butanol-HF-HCl-H₂O. The development tank and pipettes used for applying the material to the paper are of polyethylene. Inactive elements are detected by spraying with 8-hydroxyquinoline in ethanolic aq. NH₃ soln., and examining in ordinary and u.v. light, and active elements, ²³³Pa, ⁹²Zr and ⁹²Nb, by scanning the chromatogram with a Geiger-Müller counter. Results are given for R_F values of the elements named, with various concentrations of HCl and HF in the solvent. By selecting suitable solvent mixtures, the following separations can be effected—Pa-Ta-Nb, Ta-Nb, Zr-Nb, Pa-Ti, Pa-Bi, Fe-Pa, and Po-Pa (*cf.* Lederer and Vernois, *Compt. Rend.*, 1957, **244**, 2388).

R. E. ESSERY

2963. Determination of oxygen in gases. I. Kavan and J. Baše (Inst. Res. Fuels, Prague). *Paliva*, 1957, **37** (11), 385-386.—A new reagent has been proposed for the absorption of oxygen from gases. It comprises sodium dithionite (30.5 g), NaOH (14 g), pyrogallol (5 g) and Na anthraquinone-2-sulphonate (0.5 g), in 250 ml of H₂O. This reagent has ten times the absorptive capacity of alkaline pyrogallol.

J. ŽYKA

2964. Rapid determination of inorganic sulphur in various forms, particularly in sulphide ores, by the tin(II)-strong phosphoric acid reduction method. Toshiyasu Kiba, Ikuko Akaza and Nobuyuki Sugishita (Dept. Chem., Fac. Sci., Univ., Kanazawa, Japan). *Bull. Chem. Soc. Japan*, 1957, **30** (9), 972-975 (in English).—The method for the determination of sulphate S has been extended to include sulphide ores, sulphides, thiosulphates, sulphites and thiocyanates. The Sn^{II}-strong phosphoric acid reagent is prepared by heating pure H₃PO₄ (d 1.7), while a stream of air is drawn over the surface, until a thermometer in the liquid reads 300°; SnCl₂·2H₂O (50 g) is then heated with 250 g of this acid; the product may be stored in a closed vessel. For analysis, the sample (containing 20 mg of S) is evaporated to dryness with 0.5 ml of satd. Ba(OH)₂ soln. in a round-bottomed flask, and treated with 10 ml of the reagent. The liquid is heated in a stream of purified CO₂ until white fumes appear, and the H₂S formed is swept out into two bubblers containing 40 and 20 ml of 4 or 8% Zn acetate soln. The contents of the bubblers are poured into 20 ml of 0.02 N iodine, and titrated with 0.02 N Na₂S₂O₃. With thiosulphates, sulphites and thiocyanates, preliminary oxidation with a few drops of bromine water is necessary. The method is compared with Lunge's gravimetric method for various sulphide ores; the reproducibility is similar for the two methods, but the present method gives very slightly higher results which are believed to be more nearly correct. The method is checked with pure sodium and potassium salts.

A. B. DENSHAM

2965. Precipitation of sulphur as barium sulphate in the presence of orthophosphate ions. K. R. Kar and N. Nath (Dept. of Chem. and Phys., Delhi Univ., India). *J. Sci. Ind. Res., B, India*, 1957, **16** (12), 563-566.—By means of ³²P, a study has been made of the adsorption of PO₄³⁻ during the pptn. of S as BaSO₄. It is found that the minimum amount of PO₄³⁻ is carried down under the following conditions—(i) low pH (\approx 1.0); (ii) by dropwise addition of BaCl₂; (iii) by keeping all soln. at about 90°; (iv) by ageing of the ppt. in contact with the mother liquor for not more than 24 hr.

C. A. SLATER

2966. The determination of sulphur compounds in mixtures, with ferricyanide and osmium tetroxide as catalyst. F. Solymosi and A. Varga (Inst. Inorg. and Anal. Chem., Univ., Szeged, Hungary). *Anal. Chim. Acta*, 1957, **17** (6), 608-609 (in German).

—By means of three oxidation reactions several inorganic sulphur compounds can be determined in the presence of each other. (i) Sulphite, bisulphite, pyrosulphite, sulphide, dithionite, thiosulphate and tetrathionate (after decomposing into sulphite and thiosulphate) are instantly and completely oxidised to sulphate by ferricyanide, in 4 to 5 N NaOH at 50° to 60° with osmium tetroxide as catalyst. If the titration is rapid, atmospheric O interferes only with dithionite and tetrathionate, this being avoided by working in an atmosphere of N. The end-point can be detected by dead-stop or potentiometric methods. (ii) At room temp. and in 0.2 to 1.0 N NaOH, ferricyanide oxidises dithionite only to sulphite, and the reaction is not affected by large amounts of thiosulphate, sulphite and thiocyanate. (iii) Iodine oxidises dithionite and sulphite to sulphate, and thiosulphate to tetrathionate. Successive application of these three oxidation reactions permits the successive determination of sulphite and thiosulphate, of tetrathionate and thiosulphate, and of dithionite, sulphite and thiosulphate, when present together.

R. E. ESSERY

2967. Note on the detection of sulphate ions on paper chromatograms. J. A. C. Frugoni (Fac. de Quim. y Farm., Montevideo, Uruguay). *J. Chromatography*, 1958, **1** (1), 90-91 (in English).—When chromatograms are dried in an air oven, a black spot is formed where H₂SO₄ remains after the solvent has evaporated. By using Whatman No. 1 paper, developing by ascending chromatography with butanol-N HCl for 8 hr. and immediately drying in an oven at 105°, a dark spot is given with 20 μ g of H₂SO₄, and as little as 5 μ g can be detected under u.v. light. Nitric and phosphoric acids develop fluorescent and dark spots, respectively, which can be distinguished from the H₂SO₄ spot by their R_F values. Chromatograms should not be developed for more than 8 hr. Those left overnight give uniform darkening of the sheet, as also do chromatograms left to dry overnight. The reaction is due to free H₂SO₄, and, when alkali or alkaline-earth sulphates are treated, the cation remains in the region of R_F 0 to 0.1. The fluorescence fades with time, but the dark spots appear to be stable.

R. E. ESSERY

2968. Simple determination of sulphate by dissolution of barium sulphate with EDTA. Koichi Mukai and Koichi Goto (Res. Lab., Nippon Keikinzoku Co., Kambara, Shizuoka Prefecture). *Japan Analyst*, 1957, **6** (11), 732-733.—Sulphate ions (< 100 mg) are pptd. as BaSO₄ by the usual method, and dissolved in twice the equiv. of EDTA soln. (pH 11) by gentle heating. The excess of EDTA is titrated with 0.05 M BaCl₂ (phthalein complexone indicator). Interference resulting from foreign ions that form EDTA complexes under the given conditions is thus eliminated. The results compare favourably with those obtained by the gravimetric (BaSO₄) and the ordinary volumetric method involving EDTA titration of the excess of Ba²⁺.

K. SAITO

2969. Determination of sulphate by means of a metal-polyphosphate reduction method. Susumu Suzuki, Kenji Harimaya, Nobuo Tsuji and Noriko Yamaoka (Inst. Chem., Kinki Univ., Fuse, Osaka,

Japan). *Bull. Chem. Soc. Japan*, 1957, **30** (7), 771-774 (in English).—The determination of S in K_2SO_4 , $PbSO_4$, $BaSO_4$ and Na_2SO_3 , by reduction with Ti, Cr, Mn, Mo or W dissolved in H_3PO_4 , and absorption of the H_2S evolved in an aq. soln. of iodine in KI, followed by titration with $Na_2S_2O_3$, has been investigated. The reduction is carried out in a stream of CO_2 in a glass flask at $\approx 200^\circ$ or in a porcelain boat in a silica tube between 700° and 900° . Pyrophosphates, triphosphates and hexametaphosphates may be used as diluents. Experimental details are given for the various systems.

A. B. DENSHAM

2970. Indirect flame-photometric determination of sulphate ions. F. Burriel-Marti, J. Ramirez-Munoz and M. L. Rexach-M. de Lizarduy (Fac. of Sci., Univ., Madrid, Spain). *Anal. Chim. Acta*, 1957, **17** (6), 559-569 (in English).—The SO_4^{2-} are determined by pptn. with a known aq. $BaCl_2$ or aq. ethanolic $SrCl_2$ soln., and measurement of residual Ba or Sr by flame photometry. The interfering effects of HCl, ethanol and various salts are studied, and curves given. Under the conditions described, with either Ba or Sr as background elements, acceptable results are given for SO_4^{2-} in the range 0 to 70 p.p.m. with Ba and 0 to 110 p.p.m. with Sr, making a blank determination without SO_4^{2-} and using correction curves to eliminate the influence of salts. In the absence of salts other than sulphates, with Ba or Sr up to 100 p.p.m. and SO_4^{2-} up to 50 p.p.m., errors rarely exceed $\pm 10\%$, reduced to $\pm 3\%$ if a blank determination is carried out. The method can be applied to the determination of SO_4^{2-} impurity in alkali-metal salts.

R. E. ESSERY

2971. Spectrophotometric method for the determination of small amounts of sulphate ions. Iwaji Iwasaki, Satori Utsumi, Ken Hagino, Toshikazu Tarutani and Takejiro Ozawa (Lab. Anal. Chem. and Geochem., Tokyo Inst. of Technol., Ookayama Meguro-ku). *Bull. Chem. Soc. Japan*, 1957, **30** (8), 847-851 (in English).—This method of determining 0.3 to 100 p.p.m. of SO_4^{2-} in soln. comprises treatment of the sample with a suspension of $BaCrO_4$ (2.5 g of $BaCrO_4$ in 200 ml of water, 0.5 M in acetic acid and 0.01 M in HCl), centrifuging, and spectrophotometric measurement of the CrO_4^{2-} .

A. B. DENSHAM

2972. Determination of thiosulphates and thioyanates in baths for thermal sulphiding of metals. F. K. Baev, R. I. Frenkel' and Z. I. Storozhenko (Rostov State Univ.). *Zavod. Lab.*, 1957, **23** (12), 1428-1429.—The sample (2 g) is dissolved in 10 ml of a 15% soln. of $ZnSO_4 \cdot 7H_2O$, and the diluted soln. (200 ml) is filtered from ZnS and S after 2 or 3 min. An aliquot (20 ml) is titrated with 0.04 N iodine in the presence of starch to give the content of $Na_2S_2O_3$. A further sample (2 g) is dissolved in water (200 ml) and an aliquot (20 ml) is treated with 5 ml of 10% H_3PO_4 soln. and then with bromine water until a colour stable for 30 sec. appears. Saturated phenol soln. (1.5 to 2.5 ml) is added, followed after 10 to 15 min. by 5 ml of 30% KI soln. After a further 15 to 20 min. the liberated iodine is titrated with 0.05 N $Na_2S_2O_3$ to give the content of KSCN.

G. S. SMITH

2973. Oxine complex of molybdenum. D. V. Ramana Rao (Ravenshaw Coll., Cuttack, India). *Anal. Chim. Acta*, 1957, **17** (6), 538-540 (in English).—It is shown that the quant. pptn., under defined

conditions, of Mo with oxine as $MoO_4(ox)_2$ (ox = oxine), previously reported as taking place in the pH range 3.3 to 7.6, does not occur at a pH > 2.24 . In the determination of other metals, masking the Mo by means of EDTA at high pH is unnecessary, the high pH itself being sufficient.

R. E. ESSERY

2974. A gravimetric micro-method for the determination of molybdenum alone or in the presence of other elements. P. Spacu and C. Gheorghiu (Lab. Inorg. and Anal. Chem., Univ. "C. I. Parhon," Bucharest, Romania). *Z. anal. Chem.*, 1958, **169** (3), 209-212.—The method described previously (cf. *Comun. Acad. Rep. Populare Romine*, 1955, **5**, 853) for the gravimetric determination of Mo, in which $[Cr(NH_3)_4Cl][MoS_4]$ is pptd. by the interaction of a thiomolybdate and $[Cr(NH_3)_4Cl]Cl_2$ (I), has been adapted to micro quantities. Interference is caused by Be, Cd, Hg, Sn, Ti, Sb, Bi and U, but not by salts of Na, K or ammonium. Alkaline-earth metals, Mg, Zn, Ni, Co, Mn, Al and vanadates are masked with EDTA; Fe and Cu with KCN; tungstate with ammonium tartrate; Pb by pptn. as PbS. Directions are given for the preparation of I. Procedure—Add a few drops of aq. NH_3 to the soln. of ammonium molybdate (0.1 to 3 ml containing about 2 mg of Mo per ml) in an Emich micro filter-beaker, and treat with H_2S until the soln. is red. Add excess of a conc. soln. of I in aq. NH_3 , shake for 3 to 5 min. and filter. Wash the ppt. successively with a 0.08% soln. of I in dil. aq. NH_3 (few drops), 95% ethanol (1.5 ml), absolute ethanol, and ether, dry for 5 min. in a vacuum-desiccator and weigh.

A. R. ROGERS

2975. Determination of metals with a standard solution of potassium ferrocyanide. X. Determination of molybdenum. Yoshio Fujita (Dept. of Applied Chem., Fac. of Engng, Osaka Univ., Miyakojima-ku). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (12), 1757-1761.—The titration of MoO_4^{2-} with $K_4Fe(CN)_6$ was studied at various pH values and a stoichiometric relationship (cf. Ramana Rao, *Curr. Sci.*, 1953, **22**, 237) was obtained at pH 1.2 to 2.6 for 2 to 40 mg of Mo per 50 ml. The end-point is best indicated potentiometrically. Ions that produce insol. salts with MoO_4^{2-} or $Fe(CN)_6^{4-}$ cause interference.

K. SAITO

2976. Spectrophotometric determination of molybdenum as the quercetin complex in a benzoin α -oxime - chloroform - ethanol medium. G. Goldstein, D. L. Manning and O. Menis (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 539-542.—Molybdenum in slurries of ThO_2 , soln. of $UO_2(SO_4)_2$ and samples of steel can be determined, in ≈ 30 min., by extraction from dil. HCl soln. into a 0.1% soln. of benzoin α -oxime in $CHCl_3$, followed by addition to an aliquot of the organic phase of a 0.1% soln. of quercetin in ethanol. The extinction of the yellow Mo-quercetin complex is then measured at $420 m\mu$ in a 1-cm cell (for concn. of Mo of 0.6 to 1.8 μg per ml) or a 5-cm cell (0.12 to 0.36 μg per ml). The concn. of ethanol in the final soln. should be $\approx 50\%$ (v/v); only VO_3^- and WO_4^{2-} interfere seriously. The error is within $\pm 3\%$.

W. J. BAKER

2977. Rapid luminescence determination of uranium in solutions. A. F. Fioletova. *Zhur. Anal. Khim.*, 1957, **12** (6), 718-719.—A determination of U is based on the fluorescent bead test (Northup,

Ind. Eng. Chem., Anal. Ed., 1945, **17**, 664) by the use of a set of standard beads. The error is $\pm 10\%$ of the content. G. S. SMITH

2978. Studies on β -diketone - uranyl chelate compounds. IV. Spectrophotometric determination of the uranyl ion with β -diketones. Yasuhiro Yamane (Pharm. Inst., Medical Fac., Tokyo Univ., Hongo, Tokyo). *J. Pharm. Soc. Japan*, 1957, **77** (4), 400-403.—Like dibenzoylmethane (I) (cf. Yoe *et al.*, *Anal. Abstr.*, 1954, **1**, 80), benzoylacetone, benzoyl-isonicotinoylmethane, benzoyl-2-furoylmethane (II), and *o*-, *m*- and *p*-methoxydibenzoylmethane produce chelate compounds with UO_2^{2+} , which exhibit max. absorption at 375, 400, 404, 400, 400 and 403 $\text{m}\mu$, respectively. II gives the greatest molar extinction coeff. and appears to be superior to I for the determination of UO_2^{2+} ($< 120 \mu\text{g}$ per 10 ml). Pptn. of the chelate takes place in $< 40\%$ ethanol in water. The optimum pH is 5.6 to 7.6. The sample soln. (5 ml) of this pH is made up to 10 ml with II (0.2% in ethanol) (1.0 ml) and 99% ethanol. K. SAITO

2979. Determination by neutron activation of the concentration of uranium-235 in some oxides of uranium. S. May and P. Lévêque (Centre d'Etudes Nucleaires de Saclay, France). UNESCO/ND/RIC/49, 1957, 6 pp. (in French).—The sample (5 mg) and a standard of natural U_3O_8 (5 mg) were irradiated for 5 to 15 sec. in a thermal neutron flux of $10^{18} \text{ n cm}^{-2} \text{ sec}^{-1}$. The intensities of the gamma radiations from the sample and standard were then recorded and related to the ^{235}U in the oxide. Details of the calculation are given; these include consideration of contributions to the recorded activities of products of any fast fission of ^{235}U and ^{238}U . The results quoted agree well with the mass-spectrometer values. G. J. HUNTER

2980. Determination of uranium by manganometric determination of uranium peroxide. J. Alexa (Inst. Nucl. Physics, Acad. Sci., Prague). *Chem. Listy*, 1957, **51** (12), 2254-2258.—*Procedure*—To the soln. of the sample containing $> 1.5 \text{ g}$ of U per litre add NaOH soln. (10%) (free from carbonate). Separate the ppt. by centrifuging (5 min., 2000 r.p.m.) and dissolve it in a minimum of HNO_3 (10%). Add NaOH soln. (3%) till the first turbidity appears, adjust the pH to between 2 and 3 with HNO_3 (5%) and precipitate the uranium peroxide with H_2O_2 (0.5 ml) (30%). After 30 min. separate the ppt. and wash with NH_4NO_3 soln. (3%) ($3 \times 20 \text{ ml}$), the pH of which has been adjusted to between 2 and 3 with HNO_3 . Dissolve the ppt. in H_2SO_4 (1:2) (20 ml) and titrate with 0.05 N KMnO_4 , which has been standardised against a soln. of UO_2 in HNO_3 . The interfering influence of some anions can be eliminated by separating uranium in the form of sodium diuranate before H_2O_2 is added. The method described enables U to be determined in the presence of Ag, Pb, Hg, Cu, Bi, Zn, Al, Ce, Ba, Ca, Sr, Mg, K, Se and numerous anions with an accuracy of $\pm 3\%$. Interference is caused by Ni, Cd, Sn, Sb, Fe, Co, Cr, Th, F-, $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$ and PO_4^{3-} . J. ŽYKA

2981. The masking of uranium(VI) in complexometric titrations (pH 10). E. Lassner and R. Scharf (Chem. Lab. der Versuchsanstalt der Metallwerk Plansee Ges. m. b. H., Reutte/Tirol). *Z. anal. Chem.*, 1958, **159** (3), 212-214.—In the presence of H_2O_2 as masking agent, low concn. of U^{VI}

($< 0.05\%$) do not interfere in the titration of Zn, Mg, Cd or Ca with EDTA at pH 10. The indicator, Eriochrome black T, is not attacked by H_2O_2 at room temp. A. R. ROGERS

2982. The dead-stop titration. III. Dead-stop titration, derivative polarographic titration and potentiometric polarography of halides in argentimetry with two platinum or silver electrodes. Takehisa Enoki and Katsuaki Morisaka (Osaka College of Pharm., Kitayashita, Minamikawachi-gun). *J. Pharm. Soc. Japan*, 1957, **77** (8), 841-844.—Although the platinum electrode is inactive towards potential change in argentimetric titrations, it can indicate the potential change both in dead-stop and derivative polarographic titrations in the presence of H_2O_2 (cf. *Anal. Abstr.*, 1958, **5**, 1749). The error is $< 0.3\%$, being identical with that by the use of a silver electrode.

IV. Dead-stop titration, derivative polarographic titration and potentiometric polarography of cyanide in argentimetry with two platinum or silver electrodes. Takehisa Enoki and Katsuaki Morisaka. *Ibid.*, 1957, **77** (11), 1240-1242.—In the argentimetric determination of cyanide by a similar method, a different titration curve is obtained. The use of H_2O_2 activates platinum electrodes; two inflection points are clearly observed in the dead-stop and the derivative polarographic titrations, corresponding to the disappearance of free CN^- and the termination of the AgCN formation. A similar curve was obtained with silver electrodes. A decrease in pH of the initial soln. makes the inflection points less distinctive. K. SAITO

2983. Direct titration of alkalinity in hypochlorite solutions. M. Randi (Soc. Lavorazioni Organ. Inorgan., Trento, Italy). *Chim. e Ind.*, 1957, **39** (11), 915-916.—A rapid method is described for the determination of alkalinity in hypochlorites by titration with $\text{N H}_2\text{SO}_4$, with sodium sulphobromophthalein as indicator. The high stability of the indicator makes elimination of hypochlorite ions unnecessary. C. A. FINCH

2984. Determination of chlorine dioxide in solution. I. E. Flis and M. K. Bñnyaeva (Leningrad Technol. Inst.). *Zhur. Anal. Khim.*, 1957, **12** (6), 740-743.—The method is based on the reaction of ClO_2 with H_2O_2 in alkaline soln. and the iodimetric determination of the chlorite that is formed. G. S. SMITH

2985. Flame-spectrochemical analysis. V. Determination of manganese. Shigero Ikeda (Inst. for Iron, Steel and other Metals, Tohoku Univ., Katahira-cho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (7), 913-917.—Various factors affecting the Mn line at 403.4 $\text{m}\mu$ in the oxy-hydrogen flame are examined in connection with the analysis of ferromanganese and manganese steel. The intensity of emission decreases with increasing amount of HCl, HNO_3 and H_2SO_4 (the extent increasing in this sequence), but remains constant in $> 0.01 \text{ N}$ acid. Addition of HClO_4 , of methanol and of acetic acid increases the intensity, to an extent that increases with concn. Alkali- and alkaline-earth-metal ions increase the intensity, whilst heavy-metal ions (Cr, Al, Fe, Cu and Ni) decrease it, but the extent is constant within a certain range of concn. Ferromanganese (0.1 g) is dissolved in HCl (1 + 1, 20 ml), oxidised with as small an amount of HNO_3 as possible and

diluted to 500 ml. The intensity of the background (fairly strong in the presence of Fe) remains constant at 401 to 406 m μ (slit width 0.02 to 0.06 mm), whilst the Mn line is not observed at 401 and 405 m μ . K. SAITO

1986. **Determination of sulphate ions in manganese dioxide produced by electrolysis.** Ichiro Muraki, Hiroshi Kondo and Tomoko Tanabe (Developing Dept., Tokyo Denkikagaku Kogyo Ltd., Kosai, Hamana-gun, Shizuoka Prefecture). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1957, **60** (9), 1096-1098.—The pptn. of more than 20 mg of SO_4^{2-} from HCl soln. of electrolytic MnO_2 with $\text{Pb}(\text{NO}_3)_2$ is best achieved at pH 3 to 5 in the presence of 10% of ethanol and in a soln. <0.05 M in MnCl_2 . An increase in the concn. of MnCl_2 increases the solubility, whilst the presence of >20% of ethanol causes pptn. of PbCl_2 . The addition of Na_2SO_4 is recommended. The ppt. is dissolved in ammonium acetate and polarographed by the usual method. *Procedure*—Dissolve the sample (containing 0.5 to 3% of SO_4^{2-} , 0.5 g) in HCl (1 + 1, 10 ml), dilute to 160 ml and adjust the pH to between 3 and 5. Add Na_2SO_4 soln. (0.05 M, 5 ml), ethanol (20 ml) and $\text{Pb}(\text{NO}_3)_2$ (0.1 M, 15 ml), warm, and filter. Dissolve the ppt. in 3 N ammonium acetate (50 ml), add gelatin soln. (0.02%, 2 ml) and make up to 100 ml. K. SAITO

1987. **An electrolytic process for the concentration of iron in a solution.** P. Deschamps (Lab. de Chim., Fac. des Sci., Paris). *Chim. Anal.*, 1957, **39** (9), 329-330.—The total Fe in ≈ 1 litre of soln. containing salts of alkali or alkaline-earth metals (e.g., natural waters) can be determined by the slow electro-deposition of $\text{Fe}(\text{OH})_2$ inside a collodion membrane [20% (v/v) cellulose acetate in acetone] on the platinum-wire cathode. A small amount of KCl and K H tartrate soln. ($\approx N$) is added to maintain the pH at ≈ 3.5 and to complex the Fe; a current of ≈ 10 to 15 mA at 10 to 15 V is passed through the soln. (in a 1-litre cell) for ≈ 15 hr. The collodion film is removed from the wire and heated with a min. vol. of HNO_3 ; the soln. of Fe^{3+} is reduced with hydroxylamine and the Fe^{2+} are determined spectrophotometrically as the 1:10-phenanthroline complex. W. J. BAKER

1988. **Colorimetric determination of iron in phosphoric acid and its salts.** M. Grat-Cabanac (Fac. des Sci., Toulouse, France). *Anal. Chim. Acta*, 1957, **17** (6), 588-589 (in French).—In the presence of H_3PO_4 and aliphatic hydroxides, the reduction of Fe^{3+} by hydroxylamine, before its colorimetric determination with 2:2'-dipyridyl or 1:10-phenanthroline, is very slow. Dithionite is recommended as the reducing agent. By operating at pH 5 to 6, the colour attains a maximum in 1 hr., and in this range formation of S from excess of reagent does not occur. Precipitation of Ca and Al is prevented by addition of 1% of citric acid. R. E. ESSERY

1989. **Direct-reading analysis of steel solutions using a reservoir-cupped centre-post electrode.** L. C. Flickinger, E. W. Polley and F. A. Galletta (Youngstown Sheet and Tube Co., Ohio, U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part 1), 502-503.—In the direct-reading spectrometric procedure described, a reservoir-cupped centre-post electrode is used as the lower electrode and a 120° cone-shape

carbon rod as the upper one, fresh soln. being supplied to the 3-mm gap from the reservoir, thus ensuring very high sensitivity. Spark exposure is 8 sec. (after a 3-sec. pre-burn), excitation voltage is 13,000 V with 7.5 r.f. amp. at the gap. A fresh set of electrodes is used for duplicate analyses, and a high rate of air-flow through the arc-stand is essential. Rapid and accurate determinations can be made of Mo (0 to 0.5%), Si (0 to 0.5%), Cu (0 to 0.8%), Ni (0 to 1.3%), Mn (0 to 1.8%), Cr (0 to 1.4%) and Pb (0 to 0.4%), with mean deviation from the chemical values ranging from 0.013 to 0.045 (≈ 70 analyses of each element). From 0.001 to 0.1% of acid-sol. Al may also be determined (mean deviation 0.003%). The method is most suitable when available drillings are limited (sample soln. is 1 g in 25 ml). W. J. BAKER

1990. **Methods of determining gases in ferrous metals.** Z. M. Turovtseva. *Zavod. Lab.*, 1957, **23** (12), 1432-1436.—Methods for the determination of gases in steel by vacuum fusion, of oxygen by fusion in an atmosphere of argon, of oxygen in carbon steel by means of a d.c. arc, and of oxygen in iron by the isotope method, are reviewed. (29 references.) G. S. SMITH

1991. **Determination of gases in steel by vacuum heating.** Yu. A. Klyachko, L. L. Kunin, E. M. Chistyakova and N. S. Larichev (Central Sci. Res. Inst. of Ferrous Metallurgy). *Zavod. Lab.*, 1957, **23** (12), 1410-1412.—With samples containing adsorbed water the apparent content of H obtained by vacuum extraction can be high, owing to reaction of the metal with H_2O . Conversely, reaction of H with oxides can yield low results. Thus it is important to reduce to a minimum the amount of time of contact between the metal and the separated gases. Apparatus to achieve this object is described. G. S. SMITH

1992. **Rapid method of isolating the carbide phase in steel.** O. S. Spiridonova and T. I. Bezuglova. *Zavod. Lab.*, 1957, **23** (12), 1412-1413.—The sample is treated electrolytically in a soln. containing 5 g of citric acid in N KCl at room temp., without a diaphragm, for 40 to 60 min. at a c.d. of 0.02 to 0.03 amp. per sq. cm. The sample with a carbide layer is washed by dipping it successively in several beakers containing water saturated with CO_2 . The last wash-liquid is tested for the absence of Cl $^-$ and Fe. The carbides are then completely separated by electrolytic dissolution in 50% NaOH soln. at a c.d. of 0.1 to 0.5 amp. per sq. cm. for 1 to 2 min. The sample is washed, dried and weighed. The carbides are dissolved in H_2SO_4 and HNO_3 , and the soln. is analysed for Cr, Mn and Fe. G. S. SMITH

1993. **Determination of carbon by combustion of non-alloy steels.** R. Boulin and E. Jaudon (IRSID, Saint-Germain-en-Laye, France). *Chim. Anal.*, 1957, **39** (12), 463-466.—By means of the apparatus and procedure illustrated and described, a statistical study of results has been made for the gravimetric determination of CO_2 by absorption with soda-asbestos, at combustion temperatures from 1200° to 1400° and oxygen flow-rates from 200 to 600 ml per min., sweeping being continued for 10 min. after the end of the combustion, indicated by stabilisation of the flow-meter. Under the conditions given, the optimum temp. was 1275° and the best rate of flow 400 ml per min. These results may

not be directly transferable to other installations, but the attention of operators is drawn to the importance of the two variables studied.

R. E. ESSERY

2994. Photometric determination of silicon in iron and steel. II. An improved method involving the use of molybdenum blue. Kiichi Narita (Development Dept., Kobe Seiko-sho, Nada-ku). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (9), 1367-1372.—Molybdenum blue produced by reduction of molybdosilicate with 1-amino-2-naphthol-4-sulphonic acid (I) and Na_2SO_3 exhibits absorption max. at 820 $\text{m}\mu$, at which point the absorption of the Fe-tartrate complex is small. The blue colour is stable for 2 hr.; in the presence of tartrate no interference results from As and P. The influence of coloured ions is eliminated by the use of a similarly treated sample soln. for the reference soln., or by the removal of the ions by electrolysis with a mercury cathode. The working curve is linear for <0.1 mg of Si per 100 ml. *Procedure*—Dissolve the sample (0.002 to 0.2%, 5 g) in 6 N H_2SO_4 (27 ml) and H_2O_2 (15%, 10 ml), boil and add 1% KMnO_4 until MnO_2 begins to precipitate. Dissolve this with a few drops of H_2O_2 , boil and centrifuge with a small amount of filter-pulp in a platinum tube. Wash the residue with 1% H_2SO_4 , ignite it and fuse the ash with Na_2CO_3 (0.5 g). Dissolve the melt, neutralise and combine it with the main soln. and the washings, and make up to 100 ml. Take two 10-ml portions and dilute each to ≈ 20 ml. To the one add 10% ammonium molybdate soln. (4 ml) then, after 10 min., 20% ammonium tartrate soln. (4 ml) and I soln. (0.5 g in 250 ml of water containing 35 g of $\text{K}_2\text{S}_2\text{O}_8$ and 6 g of Na_2SO_3) (5 ml) and make up to 100 ml. To the other add ammonium tartrate soln. (20%, 4 ml), then ammonium molybdate soln. (10%, 4 ml) and I soln. (5 ml), and dilute to 100 ml (reference soln.). Measure the extinction at 820 $\text{m}\mu$ after 10 min.

K. SAITO

2995. A source of error in the determination of nitrogen by the wet method in special steels. R. Castro, J. Allemand and R. Poussardin (Lab. de Recherches des Acieries d'Ugine, Savoie, France). *Anal. Chim. Acta*, 1957, **17** (6), 530-534 (in French).—High results in the Kjeldahl method for the determination of N in ordinary and special steel, even when the blank is small or absent, are ascribed to the simultaneous presence of Mo (even in small proportions) in the steel, and NO_3^- in the HCl used to dissolve it. The acid should be tested with a specimen of very low content of N, e.g., electrolytic Fe, in the presence and absence of 0.1% of Mo. The difference between the two results should be negligible. If not, the acid should be discarded, or distilled before use. R. E. ESSERY

2996. Photometric determination of tungsten in steel and titanium alloys with dithiol. L. A. Machlan and J. L. Hague (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *J. Res. Nat. Bur. Stand.*, 1957, **59** (6), 415-420.—*Procedure for steel*—The sample (0.1 to 0.2 g) is dissolved in a warm mixture of HCl and HNO_3 (3:1), the soln. is evaporated to fuming with a mixture of conc. H_2SO_4 , 85% H_3PO_4 , and 70% HClO_4 , and is then cooled and diluted to 100 ml with dil. H_2SO_4 (1+3). To an aliquot (≈ 50 μg of W) is added dil. H_2SO_4 (1+3) saturated with SO_2 followed, after heating to $\approx 35^\circ$, by a 0.2% soln. of dithiol. Molybdenum and other interfering elements are then removed by

extraction into CHCl_3 ; the acid phase is filtered to remove Cu, other insol. complexes and any occluded Mo. After heating the soln. to remove SO_2 and residual CHCl_3 , the W-dithiol complex is formed, and the colour is developed at 100° , by addition of HCl, 20% (w/v) SnCl_2 soln. (containing a microgram amount of Cu), and more dithiol soln. The complex is extracted into butyl acetate and its extinction is measured at 635 $\text{m}\mu$ in a 2-cm cell. Beer's law is valid, blanks are usually negligible, and the percentage of W can be obtained from the working curve. The error is $>0.005\%$ for 0.05 to 0.5% of W, and $\approx 0.001\%$ for $<0.05\%$ of W. *For titanium alloys*—The sample (0.2 g) is dissolved in dil. H_2SO_4 plus HF, and H_2O_2 is added before evaporation of the soln. to fuming. The procedure is then as for steel, except that 2 mg of Fe [as $\text{Fe}_2(\text{SO}_4)_3$ soln.] is added initially to the suitable aliquot and the filtration step is omitted. Errors up to ± 0.2 μg on 10 μg and -1.8 μg on 50 μg of W were found.

W. J. BAKER

2997. High-frequency titration. XVII. High-frequency titration [of nickel] involving chelation. Kiyoshi Takiura, Masaichiro Masui and Terumi Watanabe (Pharm. Fac., Osaka Univ., Toyonaka). *Japan Analyst*, 1957, **6** (11), 700-706.—The high-frequency titration (for apparatus, cf. Masui, *J. Pharm. Soc. Japan*, 1953, **73**, 921; 1954, **74**, 530) of Ni with dimethylglyoxime (I), 8-hydroxyquinoline (II), dithizone (III) and 1-nitroso-2-naphthol (IV), of Cu with I and II, and of Co with III and IV was studied by three methods: back-titration of the excess of the reagent with Na methoxide in a mixture of methanol and benzene (1+2, by vol.), and back- and direct titration of the reagent in an aq. soln. The first method provides the most distinctive titration curve, but difficulty is encountered in bringing the metal ions into the non-aq. layer. The last method is applicable only to I and II. The second method thus appears to be suitable for general use. Most of the error results from adsorption.

K. SAITO

2998. Apparatus and technique for multiple tests by the confined-spot method of colorimetric analysis. Application to field estimation of nickel and copper. J. H. McCarthy, jun., and R. E. Stevens (U.S. Geol. Survey, Denver, Colo., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 535-538.—By utilising the increasing pull caused by the gradual fall of water-level in a tank, the apparatus described and illustrated will ensure a reproducible low rate of flow of sample soln. through the reagent paper so that the same percentage of reaction products is collected each time on the confined spot. With dithio-oxamide or dimethylglyoxime reagent paper, from 0.03 to 8.5 μg of Cu or 0.06 to 6 μg of Ni can thus be determined, the respective mean coeff. of variation being 22 and 14% (6 analyses). Both sample and standard spots are stable for several months; the values differ from those obtained by the colorimetric method by $\pm 17\%$ for Cu and $\pm 30\%$ for Ni. This improvement of the Stevens-Lakin chromograph (*U.S. Geol. Survey*, 1949, *Circ.* 63) is useful in geochemical prospecting.

W. J. BAKER

2999. Analysis of metallic nickel. IX. Determination of zinc. Shigeru Yokosuka (Besshi Mine Office, Sumitomo Mining Co., Niihama, Ehime Prefecture). *Japan Analyst*, 1957, **6** (7), 431-435.—Metal ions (Mn, Fe, Co, Ni, Cu, Pb, Cd, Bi, Sn, Au, Ag and Hg) causing interference with the extraction

of Zn ($>0.0001\%$ in Ni) with dithizone (I) in CCl_4 , are masked by the addition of ammonium acetate, $\text{Na}_2\text{S}_2\text{O}_3$, Na K tartrate and KCN. A large excess of CN^- (>2 ml of 50% soln. for $<16 \mu\text{g}$ of Zn and <0.5 g of Ni) retards the extraction. The working curve is linear for $<16 \mu\text{g}$ of Zn in the CCl_4 layer. The Zn - I soln. in CCl_4 remains unchanged for 30 min. The deviation is $<3\%$. The time taken for an estimation is ≈ 3 hr. *Procedure*—Dissolve the sample (5 g) in HNO_3 (1 + 1, 40 ml) and neutralise a portion (corresponding to 0.1 to 0.5 g of the sample) with aq. NH_3 soln. Add ammonium acetate soln. (20%, 10 ml), $\text{Na}_2\text{S}_2\text{O}_3$ soln. (50%, 5 ml), Na K tartrate soln. (10%, 2 ml) and KCN soln. (20%, calculated equiv. amount). Adjust the pH to between 5.7 and 7.0 with acetic acid (1 + 1) and shake with CCl_4 soln. of I (5 mg per 100 ml). Dilute the CCl_4 layer to 20 ml and wash with NaHS (1% NaOH soln. is saturated with H_2S and the supernatant soln. is diluted 20 times) (3×15 ml) and water. Measure the extinction at 530 $\text{m}\mu$.

X. Determination of cobalt. Shigeru Yokosuka. *Ibid.*, 1957, 6 (11), 690-695.—The potentiometric titration of Co (Chepik, *Zavod. Lab.*, 1947, 15, 1470; Ivanova, *Ibid.*, 1946, 12, 624; Tomicek, *Chem. Listy*, 1942, 33, 44) in nickel was examined. The amount of aq. NH_3 soln. was found to have little effect in the presence of ≈ 50 ml of M ammonium citrate for 15 mg of Co. The presence of Mn (>0.2 mg for 5 mg of Co) increases the results, whilst that of <10 mg of W^{VI} and Mo^{VI} , <100 mg of Zn, Sb, Cr, Cu, Bi, Cd, Sn^{II} and Sn^{IV} , Al, Fe and As^{V} , and <10 g of Ni does not cause interference. The extraction of the thiocyanate complex of Co with ethyl acetate - benzene (5 + 1) in the presence of phenazone (Sudo, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1953, 74, 658) is incomplete in the presence of >0.5 g of Ni. By increasing the amount of NH_4SCN (3%, 15 ml), phenazone (10%, 5 ml) and oxalic acid (15%, 15 ml), <0.5 mg of Co is satisfactorily determined in 2 g of nickel. Cobalt (0.1 to 2%) in nickel (sulphate soln.) can also be determined spectrographically (a.c. arc, 220 V, 7 amp.) by the multi-line method (Co 3044-01 - Ni 3145-70, 3105-47, 3045-01, 3145-70 \AA) on a carbon electrode.

XI. Determination of purity. (1). Fundamental experiments. Shigeru Yokosuka. *Ibid.*, 1957, 6 (11), 695-700.—The electrolysis of Ni (0.5 to 2 g) in an ammoniacal soln. was examined with reference to the source of abnormal over-deposition. Occlusion of H in low-temp. electrolysis is not the only source. The loss of platinum anode increases with increasing concn. of NH_3 , but the amount of Pt depositing on the cathode remains almost unchanged. The use of depolarisers such as Na_2SO_3 , hydroxylamine hydrochloride or hydrazine sulphate was not satisfactory. The determination of Ni (Rollet, *Compt. Rend.*, 1926, 183, 212; Mitcher and Mellon, *Ind. Eng. Chem., Anal. Ed.*, 1945, 17, 380) and Co (Sudo, *loc. cit.*) in the electrolytic soln. was also examined.

XII. Determination of purity. (2). Elucidation of the over-deposition. Shigeru Yokosuka. *Ibid.*, 1957, 6 (12), 753-756.—This phenomenon was further examined at various current densities (0.1 to 2 amp. per sq. dm). At a high temp. ($\approx 75^\circ$), Pt is deposited on the cathode when the Ni concn. in the electrolyte is <0.1 mg per 150 ml, the rate increasing with increase in current density (e.g., 0.1 mg per 20 min. at 2 amp. per sq. dm; 0.1 mg per 180 min. at 0.2 amp. At a low temp. ($\approx 30^\circ$), occlusion of H takes place to an increasing extent with

increasing current density and amount of Ni. The optimum conditions are—sample, 1 g; current, 0.1 amp. per sq. dm; temp. 20° to 30° ; duration, 24 hr.

XIII. Determination of purity. (3). Removal of impurities and the method of determination. Shigeru Yokosuka. *Ibid.*, 1957, 6 (12), 756-761.—Copper, Zn and Co which are deposited together with Ni in the electrolysis of high-purity nickel in an ammoniacal soln. [24 g of $(\text{NH}_4)_2\text{SO}_4$ and 25 ml of aq. NH_3 soln.] are determined spectrophotometrically and deducted from the result. Any Ni remaining in the electrolyte is determined photo-metrically with dimethylglyoxime (Mitcher *et al.*, *loc. cit.*) and added to the result. For samples of a lower grade ($<99.94\%$ of Ni plus Co), the elements of the H_2S group are pptd. in 0.3 N H_2SO_4 soln., after reduction with hydrazine sulphate in conc. H_2SO_4 ; Mn is pptd. by boiling with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (2 g for 0.05 mg of Mn) in an ammoniacal soln. The resulting soln. is electrolysed under similar conditions. The overall deviation is $\approx 0.005\%$ for high-purity samples and $\approx 0.01\%$ for less pure samples. K. SAITO

3000. Co-precipitation of nickel and zinc with aluminium hydroxide by polarographic methods. P. N. Kovalenko (Rostov-on-Don State Univ.). *Zhur. Prikl. Khim.*, 1957, 30 (12), 1769-1776.—With increase in the concn. of aq. NH_3 up to a certain limit the co-pptn. of Ni and Zn with $\text{Al}(\text{OH})_3$ becomes insignificant, but small amounts of Al dissolve. With increase in the concn. of NH_4Cl , the concn. of aq. NH_3 can be reduced sufficiently for the dissolution of $\text{Al}(\text{OH})_3$ to become insignificant and the co-pptn. of Ni and Zn to become insignificant because of exchange adsorption with NH_4^+ . The adsorption of Ni and Zn by $\text{Al}(\text{OH})_3$ obeys empirically the Freundlich isotherm. The optimum pH for the pptn. of $\text{Al}(\text{OH})_3$ is ≈ 5 . G. S. SMITH

3001. Flame-spectrophotometric method for the determination of nickel and boron in plating solutions. D. E. Fornwalt (Pratt & Whitney Aircraft Div., Canel Operations, East Hartford, Conn., U.S.A.). *Anal. Chim. Acta*, 1957, 17 (6), 597-603 (in English).—The determination of Ni and B in methanol-water (1:1) has been studied with reference to mutual interference. Boron has no effect on the luminosity of the Ni line at 352.5 $\text{m}\mu$, but Ni increases the luminosity of the B band-system at 518 $\text{m}\mu$. The use of methanol-water as solvent increases the flame intensity of both B and Ni by a factor of ≈ 3 . For analysis, 250 μl of the sample soln. is mixed with 5 ml of methanol and diluted to 10 ml with demineralised water. The flame luminosity is read at 352.5 $\text{m}\mu$, and the Ni content obtained from a calibration curve. The flame luminosity is then read at 518 $\text{m}\mu$. From this is deducted the background luminosity due to the Ni, which is read from a second calibration curve. The remainder is the luminosity due to B, which is referred to a third calibration curve. The precision and accuracy are within 1%, and flame-photometric results agree well with those by classical procedures. R. E. ESSERY

3002. Separation by paper chromatography and spectrophotometric determination of trace amounts of cobalt, nickel, copper and zinc. W. J. Frierson, D. A. Rearick and J. H. Yoe (Agnes Scott Coll., Decatur, Ga., U.S.A.). *Anal. Chem.*, 1958, 30 (4, Part 1), 468-471.—The method includes a two-solvent separation, elution of the ions from sections of the chromatogram, and spectrophotometric

determination by conventional means. It may be applied to microgram quantities of any combination of the four elements. Several solutions of the eluted ions containing between 0.5 and 2.0 μg per litre showed recoveries of between 96 and 100%.

K. A. PROCTOR

3003. The determination of fission-product ruthenium. R. P. Larsen, L. E. Ross and G. Kesser (Argonne Nat. Lab., Lemont, Ill.). *U.S. Atomic Energy Comm.*, Rep. ANL-5810, Dec. 1957, 7 pp.—Improvements in Glendinin's procedure ("Radiochemical Studies: The Fission Products," C. D. Coryell and N. Sugarman, McGraw-Hill Book Co., 1951) have been made. The distillation from HClO_4 has been replaced by a more rapid distillation from dil. H_2SO_4 -sodium bismuthate mixture. Conditions for the quant. volatilisation and collection of the tetroxide and its reduction to the dioxide have been established. Reduction to the metal is no longer necessary. The analysis time has been halved. The coeff. of variation has been reduced from $\pm 7.3\%$ for the HClO_4 method to $\pm 2.3\%$.

N. E.

3004. Spectrographic determination of palladium in Doré metal. N. Tomingas and W. C. Cooper (Canadian Copper Refiners Ltd., Montreal East, Que., Canada). *Appl. Spectroscopy*, 1957, **11** (4), 164-166.—A globule method is described for the determination of 45 to 800 p.p.m. of Pd in Doré metal (90 to 95% of Ag, 5 to 10% of Au, 0.3 to 0.8% of Cu). A Hilger B.N.F. controlled source unit is used in conjunction with a Littrow spectrograph. A correction for variations in Cu content is necessary, and the effects of Au content in excess of 9% are overcome by diluting the sample with Ag. Good agreements with polarographic assays were obtained, the coeff. of variation being 3-8%. The method is applicable to any material from which the precious-metal content may be concentrated by cupellation. Silver and gold are added to the resulting bead to make its composition comparable with the Doré bead standards.

P. T. BEALE

3005. Use of oscillographic polarography in quantitative analysis. VIII. Determination of palladium, rhodium and iridium with ethylenediamine as electrolyte. P. Beran and J. Doležal (Inst. Anal. Chem., Charles' Univ., Prague). *Chem. Listy*, 1957, **51** (12), 2243-2246.—With the use of oscillographic titrations a rapid determination of Pd, Ir and Rh in a soln. of ethylenediamine sulphate (I) in the presence of Pt and Au is possible, characteristic cut-ins being obtained on the cathodic part of the curve $dE/dt = f(E)$ (Pd -1.1 V, Rh -0.3 V, Ir -0.5 V and -1.5 V). The titrations are carried out in 10 ml of M I. The concn. of the metals in the sample must not exceed 1×10^{-4} M Pt, 3×10^{-4} M Au, 1×10^{-4} M to 8×10^{-4} M Pd, 3×10^{-3} M to 7×10^{-3} M Rh, and 2×10^{-3} to 7×10^{-3} M Ir. The following combinations of metals can be determined to an accuracy within $\pm 10\%$ —Pd, Pt (1:40); Pd, Ir (1:30); Pd, Rh (1:10); Rh, Pt (1:2); Rh, Pd (1:30); Rh, Ir (1:6); Ir, Pt (1:6); Ir, Pd (1:50); Ir, Rh (1:1); Pd, Rh or Ir in the presence of Au (1:100).

J. ZÝKA

3006. Rapid analytical methods for fuel ash. I. Photometric determination of silicon, aluminium, iron, titanium and phosphorus. W. Radmacher

and W. Schmitz (Brennstoffchem. Inst. der Ruhrkohlen-Beratung, G.m.b.H., Essen). *Brennst.-Chemie*, 1957, **38** (15-16), 225-230.

II. Determination of calcium, magnesium, sodium and potassium. W. Radmacher and W. Schmitz. *Ibid.*, 1957, **38** (17-18), 270-274.

III. Determination of copper, nickel, cobalt, zinc, manganese and vanadium. W. Radmacher and W. Schmitz. *Ibid.*, 1957, **38** (19-20), 308-312.—Details are given of the methods used by the authors.

A. R. PEARSON

3007. Rapid analysis of cement. V. Krajovan-Marjanović and Z. Pučar (Zavod. anal. kem. Tehnol., Fak. sveučilišta, Zagreb). *Kem. u Ind., Zagreb*, 1957, **6** (9), 249-253.—This rapid volumetric determination of Fe_2O_3 , Al_2O_3 , CaO , MgO and SO_2 in cement is based on the pptn. of the cation complex with 8-hydroxyquinoline (I). Silica is determined gravimetrically after pptn. with gelatin. Ferric and aluminium hydroxides are pptd. by adding aq. NH_3 and the ppt. is filtered off and dissolved in aq. acetic acid. A measured excess of I is added, and the pptd. iron complex of I is separated. Standard KBrO_3 -KBr soln. is added to the acidified filtrate, the Br formed reacts with the excess of I, and the unchanged Br is determined iodimetrically. The aluminium complex of I is pptd. by adding aq. NH_3 . Excess of I is determined as described above. After the removal of Fe^{3+} and Al^{3+} , the magnesium complex of I is pptd. at pH 5, and estimated as above. Calcium is determined as oxalate. Sulphate is determined by adding BaCrO_4 in acid soln., filtering and estimating the free chromate ions iodimetrically. The method gives results 0.5% low for Al_2O_3 (total 7.9%), and 0.5% high for Fe_2O_3 (total 3%).

P. M. SORGO

See also Abstracts—**3021.** Arsenometric determination of BrO_3^- and Fe^{4+} . **3028.** Gasometric determination of hydrazine. **3046.** Determination of tetra-ethyl lead in motor spirits. **3050.** Determination of Cu in gelatin. **3175.** Determination of HCN in air. **3177.** Determination of thiophosphoryl chloride in air. **3182.** Determination of F in water. **3183.** Determination of P in water containing polymetaphosphates. **3184.** Determination of ^{88}Sr and ^{90}Sr in water. **3185.** Determination of V in water. **3195.** Handling of microgram quantities in metal investigations. **3196.** Use of Na_3PO_4 as masking agent in volumetric analysis. **3202.** Inorganic paper chromatography. **3203.** Separation of isotopes by chromatography and electrophoresis. **3212.** Spectrochemical analysis by the evaporation method. **3214.** Spectrochemical analysis of non-metallic samples. **3217.** Electrolytic lifting of films from metals for i.r. analysis.

3.—ORGANIC ANALYSIS

3008. Organic quantitative analysis. XVIII. Micro-determination of carbon and hydrogen with cobalto-cobaltic oxide as combustion catalyst. M. Večeřa and L. Synek (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1957, **51** (12), 2266-2274.—The sample is burnt on a layer of cobalto-cobaltic oxide in a stream of O. The halogens and sulphur are absorbed on silver and the oxides of N are trapped on activated manganic oxide outside the combustion tube.

The method was checked by analysing numerous samples of difficultly combustible compounds. The apparatus and the procedure are described in detail.

J. ZYKA

3009. Determination of carbon and hydrogen. IV. The absorption of nitrogen oxide. (1). Ammonium sulphamate. Satoshi Mizukami, Tadayoshi Ieki and Nobu Morita (Res. Lab., Shionogi & Co., Imafuku, Amagasaki). *J. Pharm. Soc. Japan*, 1957, **77** (5), 552-554.—The use of ammonium sulphamate on silica gel for the reduction of NO_2 (Hussey *et al.*, *Anal. Abstr.*, 1955, **2**, 2109) was examined with various nitrogen compounds. The silica gel also adsorbs NO_2 quant., although the capacity is small (≈ 7 mg of NO_2 per 1.5 g).

V. The absorption of nitrogen oxide. (2). Tris-hydroxylamine phosphate. Satoshi Mizukami, Tadayoshi Ieki and Hiroko Kondo. *Ibid.*, 1957, **77** (5), 517-520.—The use of tris-hydroxylamine phosphate (I) on silica gel (Cross and Wright, *Anal. Abstr.*, 1954, **1**, 2107) was examined with reference to the behaviour of NO produced by the dissociation of NO_2 . It appears that the equilibrium shifts in favour of NO_2 in the absorption tube. A U-tube (diameter, 1 cm; total length, 10 cm) containing silica gel (20 mesh, 0.5 g), a mixture (1 + 1, by wt., 2 g) of silica gel (20 mesh) and I, and $\text{Mg}(\text{ClO}_4)_2$ (to fill the remainder of the tube) is connected between the absorption tubes for H_2O and CO_2 .

VI. Simultaneous determination of carbon, hydrogen and sulphur. Satoshi Mizukami, Tadayoshi Ieki and Hiroko Kondo. *Ibid.*, 1957, **77** (5), 520-523.—Stragand's method (*Anal. Chem.*, 1949, **21**, 625) for the determination of S was modified by replacing the platinum catalyst by rolled copper oxide gauze. By connecting the absorber for NO_2 , mentioned above, C, H and S can be determined simultaneously. When kept at 850° to 900° , the copper oxide gauze does not react with oxides of S, which are quant. absorbed by a rolled gauze (60 mesh, activated by electrolysis in 1% H_2SO_4) kept at 550° , without affecting the determination of C and H.

K. SAITO

3010. Direct determination of oxygen in the elementary analysis of organic substances. R. Fort. *Chim. Anal.*, 1957, **39** (9), 319-328.—The direct determination of O in oils, rubber, bitumen, tar, coke, etc., by methods based on those of Schutze (*Z. anal. Chem.*, 1939, **118**, 245) and Unterzaucher (*Ber.*, 1940, **73**, 391; *Analyst*, 1952, **77**, 584) is critically discussed. Recently developed macro- and micro-methods are reviewed according to the various modifications made in the apparatus and procedure. (See *Anal. Abstr.*, 1958, **5**, 2662).

W. J. BAKER

3011. Micro-determination of oxygen. VI. Results in routine work. Tetsuro Konô, Keiko Sato, Mizue Suzuki and Ikuko Isobe (Fac. of Agric., Tokyo Univ., Hongo). *J. Agric. Chem. Soc. Japan*, 1957, **31** (8), 587-592.—The use of hot silver gauze for the quant. absorption of iodine produced by the oxidation of CO with I_2O_5 (*Ibid.*, 1955, **29**, 942) was further studied with reference to the maintenance of the surface state of the silver and the removal of the last trace of O in the nitrogen. The former is best achieved by electrolysis (*loc. cit.*) after the gauze has been used 5 to 8 times; the latter is effected by mixing electrolytic H ($<4\%$) with the nitrogen. The error is $\pm 0.1\%$ (absolute) for samples without S; the effect of S is eliminated by increasing the length of the copper column.

K. SAITO

3012. Volumetric determination of chlorine in methylchlorosilanes and phenylchlorosilanes. Fumio Hirata and Toshio Takiguchi (Kiri College of Tech., Gumma Univ., Kirii, Gumma Prefecture). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1957, **60** (9), 1204-1206.—Methyltrichlorosilane, dimethyldichlorosilane, phenyltrichlorosilane and diphenyldichlorosilane (20 to 150 mg) are hydrolysed with 50% aq. ethanol in a sealed vessel and the Cl- are titrated with AgNO_3 in an aq. suspension. Dichlorofluorescein is the best indicator (error, $\pm 0.2\%$). The presence of ethanol and organopolysiloxanes does not cause interference.

K. SAITO

3013. A new method for the micro-determination of methoxyl groups. Minoru Fukuda (Pharm. Fac., Osaka Univ., Toyonaka). *J. Pharm. Soc. Japan*, 1957, **77** (8), 934-935.—Methyl iodide, produced by heating the sample with HI (sp. gr. 1.7; refluxed with 15 g of phenol, 0.1 g of red P and 1 g of propionic acid) in an air stream, is introduced into a combustion tube containing platinum catalyst. The iodine is trapped by silver gauze and determined gravimetrically.

K. SAITO

3014. Photometric determination of phenoxy groups in organosilicon compounds. A. P. Kreshkov and V. A. Bork (D. I. Mendeleev Chem.-Tech. Inst., Moscow). *Zhur. Anal. Khim.*, 1957, **12** (6), 764.—The sample is dissolved in 5 to 6 ml of ethanol and the soln. is heated under a reflux condenser on a boiling-water bath with 4 ml of conc. aq. NH_3 for 3 to 4 min. The ppt. is removed and washed, and the filtrate, diluted to 25 ml, is heated with 30 drops of Cl or Br water under a reflux condenser for 5 min., and its extinction is measured after cooling.

G. S. SMITH

3015. Determination of oxygenated materials as group types by infra-red absorption. E. L. Saier and R. H. Hughes (Gulf Res. & Development Co., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part 1), 513-517.—A fairly rapid method is described for the quant. determination of alcohols, acids, aldehydes, esters, ketones and ethers in a mixture. Absorbances are determined at six wavelengths and substituted into a matrix to give concn.

K. A. PROCTOR

3016. Colorimetric determination of fusel oil. I. Determination of higher alcohols in fusel oil with anisaldehyde - sulphuric acid reagent. Mikio Tomoda and Hiromichi Onozaki (Fac. of Agric., Gifu Univ.). *J. Agric. Chem. Soc. Japan*, 1957, **31** (9), 672-675.—Since vanillin- H_2SO_4 reagent (Penniman, *Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 91) gives absorption curves of different shapes with some higher alcohols, the use of an alternative aldehyde was examined. Anisaldehyde (I) gives an identical absorption (max. 580 m μ) with various alcohols, and the extinction coeff. decreases in the sequence isobutyl alcohol, isoamyl alcohol, *n*-butanol, isopropyl alcohol and *n*-propanol. The same conditions as for vanillin can be used for I.

K. SAITO

3017. Paper chromatography of methylated D-glucosamine, D-galactose and D-mannose. Shichiro Akiya and Masashi Tomoda (Kyotitsu College of Pharm., Shiba, Minato-ku, Tokyo). *J. Pharm. Soc. Japan*, 1957, **77** (6), 697-698.—Paper chromatography of partially methylated D-galactose, D-mannose and N-acetyl-D-glucosamine was studied

with a mixture of butanol, ethanol, water and aq. NH_3 soln. (40 + 10 + 49 + 1) (A), and of butanol, acetic acid and water (4 + 1 + 1) (B). By the use of B, the R_G values of the first two compounds are greater than those by the use of A, whilst those of the last derivative are greater by the use of A.

K. SAITO

3018. Infra-red identification of disaccharides. J. W. White, jun., C. R. Eddy, J. Petty and N. Hoban (Eastern Regional Res. Lab., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 506-510.—Infra-red spectra are useful for the identification of amorphous disaccharides and their acetates, as the spectra differ sufficiently to allow differentiation among closely related disaccharides. The i.r. spectra (potassium bromide disc) of ten disaccharides of D-glucose, of D-glucose and D-fructose, and of their β -octa-acetates are given over the range 650 to 1500 cm^{-1} . K. A. PROCTOR

3019. Quantitative paper chromatography of aliphatic aldehydes by hydroxamic acid method. Gaku Izumi and Yutaka Yamada (Gov. Ind. Res. Inst., Nagoya, Hirate-machi, Kita-ku). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1957, **60** (12), 1525-1527.—The chromatographic spots (descending technique, benzene-isomyl alcohol, 1 + 1) (*Anal. Abstr.*, 1958, **5**, 2252) of the hydroxamic acids are cut out, extracted with FeCl_3 (0.003% in ethanol) (at 20° for 2 hr.) and measured at 520 $\text{m}\mu$, with 0.003% FeCl_3 in ethanol as reference soln. The working curve is linear for <10 mg of acid per litre, the curves being almost identical for aliphatic aldehydes with 6 to 10 carbon atoms.

K. SAITO

3020. Paper chromatography of 2:4-dinitrophenylhydrazones of saturated aliphatic aldehydes. R. Ellis, A. M. Gaddis and G. T. Currie (U.S. Dept. Agric., Beltsville, Md., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 475-479.—Two systems are used. In the first, filter-paper impregnated with propane-1:2-diol was used, with Skellysolve C (b.p. 91° to 95°) and methanol as developer, and in the second, filter-paper impregnated with petroleum jelly, and aq. methanol as developer. The first separates the 2:4-dinitrophenylhydrazones of n aliphatic saturated aldehydes from C_1 to C_6 , and the second system those from C_1 to C_{14} . The hydrazones are identified by absorptiometric measurement of the extracted spots. Some physical constants of the hydrazones, and separation data for the two systems, are listed.

G. P. COOK

3021. Arsenometric determination of formaldehyde, formic acid, bromate and iron(II). L. G. Molnár, L. Szekeres and M. Zergényi-Balásfalvy (Inst. für allgemeine Chem. der Landwirtschaftlichen Univ., Budapest). *Z. anal. Chem.*, 1958, **159** (3), 161-164.—Bromates are determined by conversion into Br and titration with As_2O_3 according to the method described previously (*cf. Anal. Abstr.*, 1958, **5**, 70). Formaldehyde, formic acid and ferrous salts are determined by oxidation with excess of Br and titration of the excess with As_2O_3 . *Procedure*—For bromates, mix the sample (10 ml of 0.1 N soln.) with 0.5 N KBr (10 ml), dilute with H_2O (10 or 20 ml), acidify with 2 N HCl and after 10 or 15 min. titrate with 0.1 N As_2O_3 , with KI-starch soln. as indicator. For ferrous ions, mix the sample (5 or 10 ml of 0.1 N soln.) with 0.1 N KBrO_3 -KBr soln. (10 or 20 ml), acidify with 5 N H_2SO_4 (20 ml), dilute with H_2O (10 or 20 ml) and after 5 to 15 min. titrate with 0.1 N As_2O_3 . For

formaldehyde or formates, mix 0.1 N KBrO_3 -KBr (10 ml) with N HCl (20 ml) and after a few minutes add 5 N NaOH (7.5 ml); mix this soln. with the sample (5 ml of 0.1 N soln.) and H_2O (10 ml); after 30 min. acidify with 50% acetic acid (5 ml); after a further 30 min. add 10 N HCl (5 ml) and titrate with 0.1 N As_2O_3 .

A. R. ROGERS

3022. Determination of higher alkylketen dimers with bromine. Fumio Takei, Koichi Murai and Giichi Akazome (Sansuio Yushi Ind. Ltd., Yoshijima, Fushimi-ku, Kyoto). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1957, **60** (10), 1271-1273.—The use of Br in CCl_4 for the determination of the iodine value of decyl-, dodecyl-, tetradecyl- and hexadecylketen dimers was studied. Bromination is completed within 30 sec. at <20° in CCl_4 soln. of the sample. The addition of iodine or iodine bromide proceeds only very slowly. *Procedure*—Cool the CCl_4 soln. (10 ml) of the sample (0.3 to 1 g) below 20° and add 0.2 N Br (<20°, 25 ml). Add KI soln. (10%, 20 ml) and water (100 ml) after 30 sec. and titrate the excess of Br with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$.

K. SAITO

3023. Separation of volatile aliphatic acids by paper chromatography. R. Osteux, J. Guillaume and J. Laturaze (Lab. de Chim. Biol. de la Fac. de Méd. et de Pharm., Lille, France). *J. Chromatography*, 1958, **1** (1), 70-85 (in French).—Work on the separation of C_1 to C_6 volatile aliphatic acids is reviewed, and the following procedure, applicable to biological fluids and bacterial cultures, is advocated. The acids are recovered from the material by steam-distillation under specified conditions. Total acidity is determined by titration, bubbling with N throughout, but for not longer than 10 min. to avoid loss of volatile acid. A small excess of NaOH is added, the liquid evaporated to 1 ml, and treated with the calculated amount of cation-exchange resin (Permutit 50 or Amberlite IR-120), shaken and allowed to stand for 5 min. It is then filtered through absorbent cotton, and washed, into a tube containing the calculated amount of N morpholine, and a drop of pure morpholine is added in excess. Chromatography of this soln. is carried out on Whatman No. 3 paper, for straight-chain acids for 24 hr. with butanol-cyclohexane-propane-1:2-diol-aq. NH_3 (sp.gr. 0.92)-morpholine-water (30:30:10:0.7:0.07:3.5), or, for iso acids, for 4 days with benzyl alcohol saturated with 1.5 N aq. NH_3 . After drying for 10 min. at 50°, the spots are detected by spraying with a soln. of cresol red in barbitone buffer. R_F values are quoted for three solvent systems. Conc. of 0.05 μmole of formic, 0.1 μmole of acetic, propionic and butyric, and 0.15 μmole of valeric and n -hexoic acids can be detected. Mineral acids remain at the point of application, and lactic acid is found between formic and acetic acids.

R. E. ESSERY

3024. Chromatography of non-volatile organic acids. M. Traiter (Dept. of Pharm. Chem. and Biochem., Acad. Sci., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1957, **11** (10), 583-589.—The separation and identification of tartaric, oxalic, citric, malic and succinic acids by means of paper chromatography was investigated with ethanol- H_2O -pyridine, ethanol- H_2O -aq. NH_3 and n -propanol- H_2O -pyridine. The most suitable developer was n -propanol- H_2O -pyridine (15:4:1), and bromocresol green (0.05% in 96% ethanol) was used for detection. Quantitative determination of the separated acids was based on measurement of the size

of the spots. Non-volatile acids (5 to 80 μ g) isolated from plant material were determined with an error of ± 10 to 25%.

J. ZÝKA

3025. Application of chelatometry to the determination of oxalic esters and mono-ester chlorides. C. Hennart and E. Merlin (Organsynthèse, Lab. de Vitry, Seine, France). *Anal. Chim. Acta*, 1957, **17** (6), 534-537 (in French).—The compound (≈ 0.002 mole) is saponified by heating under reflux in a boiling-water bath for 1 hr. with *N* ethanolic NaOH. Chlorides of the mono-esters, which react vigorously with NaOH, are weighed in a glass cup, and this is overturned into the NaOH soln. after the condenser, previously moistened internally with NaOH and fitted with a guard-tube, has been attached. After cooling, the liquid is acidified with acetic acid, boiled to expel CO_2 , and treated with 50 ml of *M* Na acetate, followed, while boiling is maintained, by 25 ml of 0.2 *M* CaCl_2 . The cooled mixture is made up to 250 ml, filtered rapidly, and 25 ml of the filtrate is treated with 10 ml of magnesium reagent (cf. *Ibid.*, 1957, **17**, 463); the excess of Ca is back-titrated with 0.02 *M* EDTA (disodium salt), with Eriochrome black T as indicator. Recoveries of 8 oxalic esters and 2 mono-ester chlorides ranged from 99.0 to 100.3%. No interference is caused by SOCl_2 or POCl_3 .

R. E. ESSERY

3026. Colorimetric estimation of tertiary and quaternary amines. S. Sass, J. J. Kaufman, A. A. Cardenas and J. J. Martin (Army Chem. Center, Md., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 529-531.—Two methods are presented. In one, the reaction of amine with aconitic anhydride is used, and in the other the reaction of amine with chloranil. When used in conjunction, the methods can be used to differentiate between tertiary amines and amine salts or quaternary amines. The analytical wavelengths for the aconitic anhydride and chloranil methods are 500 $\text{m}\mu$ and 610 $\text{m}\mu$, respectively, and the sensitivities are $\approx 3 \mu\text{g}$ per ml and 50 μg per ml, respectively. Several mixtures of amines gave recoveries of $\approx 99\%$.

G. P. COOK

3027. Analysis of mixtures of ethylenediamine and polyethylenamines. L. Nebbia and B. Pagani (Ist. Ricerche Guido Donegani, Novara, Italy). *Chim. e Ind.*, 1957, **39** (11), 913-915.—Colorimetric analyses of small amounts of polyethylenamines in ethylenediamine and chromatographic analysis of ethylenediamine in polyethylenamines are considered. Methods based on the different solubilities and colours of the copper complexes are given, with suitable absorption curves. The accurate determination of amounts down to 0.1% of polyethylenamines in ethylenediamine and 1% of ethylenediamine in polyethylenamines is possible.

C. A. FINCH

3028. Gasometric determination of hydrazine and derivatives. H. McKennis, jun., J. H. Weatherby and E. P. Dellis (Med. Coll. of Va., Richmond, U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 499-502.—When treated with IO_3^- , hydrazine and some of its derivatives gave quant. yields of N_2 . The N_2 was measured manometrically in a Warburg apparatus, and preliminary tests showed a high degree of precision. The mean recovery of N_2 from hydrazine sulphate was 99.5%, with a standard error of $\pm 1.2\%$ (4 determinations); results for about 30 derivatives are listed. The reaction proceeded

rapidly with methylhydrazine and the monoacyl hydrazines studied, but phenylhydrazine yielded N_2 slowly. 1:2-Diacylhydrazines failed to give N_2 except after hydrolysis.

G. P. COOK

3029. Determination of ethanolamines in mixtures. J. Kubias (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1957, **51** (12), 2275-2279.—Simple methods for the determination of total basicity, specific determination of triethanolamine (I) and for the determination of monoethanolamine (II) and diethanolamine (III) are described. **Total basicity**—To 20 ml of the mixture add thymol blue (3 to 4 drops) as indicator and titrate with 0.1 *N* ethanolic HCl. **Determination of I**—To 20 ml of the sample add acetic anhydride (1 ml), mix, and set aside for 10 min. Add thymol blue (3 to 4 drops) and titrate as described above. Any large excess of NH_3 must be removed by heating the soln. before the titration is carried out. **Oxidimetric titration of II and III**—To 20 ml of H_2O and 20 ml of a satd. soln. of NaHCO_3 , add 2 ml of the sample and 10 ml of 0.0125 *M* KIO_4 . Mix and set aside for 15 min. Add 10 ml of 0.03 *N* Na_3AsO_4 and 2 ml of KI soln. (10%). After 15 min. add starch soln. and titrate with 0.02 *N* iodine. **Determination of II**—To chlorobenzene (130 ml) add 10 ml of the sample and distil (2 drops per sec.). Titrate an aliquot part of the distillate as described above.

J. ZÝKA

3030. Polarographic determination of isopropyl nitrate. A. F. Williams and J. Brooks (Res. Dept., I.C.I. Ltd., Stevenston, Ayr, Scotland). *J. Polarographic Soc.*, 1958, **1** (1), 5-7.—The wave in 0.1 *M* LiCl in methanol is optimum if the methanol is standardised to contain 5% v/v of H_2O . Nigrosine is used as max. suppressor. The $E_{1/2}$ is -1.45 V vs. the mercury pool, and the wave height is proportional to concn. Application of the method to the cathode ray polarograph is also described. Other aliphatic nitrates behaved similarly.

H. F. W. KIRKPATRICK

3031. Separation and identification of aliphatic mercaptans by chromatography of the 2:4-dinitrophenyl sulphides. J. F. Carson and F. F. Wong (U.S. Dept. of Agric., Albany, Calif.). *J. Org. Chem.*, 1957, **22** (12), 1725-1726.—The rates of movement of alkyl dinitrophenyl sulphides were found to increase in the order $\text{CH}_3 < \text{C}_2\text{H}_5 < \text{CH}_2\text{CH}_2\text{CH}_2 < n\text{-C}_3\text{H}_7 < n\text{-C}_4\text{H}_9 < n\text{-C}_5\text{H}_{11} < \text{tert.-C}_4\text{H}_9 < n\text{-C}_6\text{H}_{13}$. Mixtures of any of these derivatives could be resolved into separate distinct bands, but this could not be done with mixtures of isomeric alkyl 2:4-dinitrophenyl sulphides, with the exception of the *tert.*-butyl derivative. N. E.

3032. Turbidimetric determination of small amounts of xanthate and carbon disulphide. D. N. Finkel'shtein (Sverdlovsk Inst. of Work Hygiene and Occupational Diseases). *Zhur. Anal. Khim.*, 1957, **12** (6), 754-758.—Alkali xanthates can be determined by means of salts of Cu at pH 3.5 to 4.5 with measurements after ≈ 20 min., or of Hg at pH 3.2 to 4.0 with measurements after ≈ 45 min. following mixing of the soln. For the determination of CS_2 , the vapour is passed through a 3% soln. of NaOH in ethanol, and the xanthate is determined turbidimetrically.

G. S. SMITH

3033. Reaction of iodine in methanol with decaborane and tetraborane. A. E. Messner (Esso Res. and Engng Co., Linden, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 547-548.—Decaborane and tetraborane react instantaneously with a soln. of iodine in methanol, evolving heat and hydrogen. By back-titrating the excess of iodine with $\text{Na}_2\text{S}_2\text{O}_3$ soln., or measuring the vol. of H_2 evolved in a closed system, an approx. quant. determination of $\text{B}_{10}\text{H}_{14}$ or B_4H_{10} can be made, utilising the suggested reaction equations.

W. J. BAKER

3034. Photometric determination of silicon in ethyl silicate. E. I. Fogel'son (Likhachev Moscow Automobile Works). *Zavod. Lab.*, 1957, **23** (12), 1427.—The method is based on that for determining Si in ferrous metals (*Anal. Abstr.*, 1956, **3**, 2738). The sample (0.1 g) is treated for a few minutes with 5 ml of conc. HCl and the mixture is then stirred with 20 ml of 20% NaOH soln. to give a clear soln., which is treated with 35 ml of dil. H_2SO_4 (1:8) and diluted with water to 250 ml. An aliquot (25 ml) is mixed with 20 ml of dil. H_2SO_4 (1:8) and diluted to 250 ml, and from this soln. three 10-ml aliquots are taken, one of them to serve as a blank. These aliquots are diluted to 40 ml and two of them are treated with 5 ml of 5% ammonium molybdate soln. followed, after 3 min., by 10 ml of 3% ammonium oxalate soln. and then immediately by 5 ml of a 5% soln. of ferrous ammonium sulphate containing 20 ml of conc. H_2SO_4 per litre. The third aliquot is treated with the same reagents except the molybdate. The soln. are diluted to 100 ml and the extinctions are measured with a red filter.

G. S. SMITH

3035. Determination of silicon content of siloxanes. Tosizo Uryu, Tadashi Wada and Akira Hanyo (Res. Lab., Shinetsu Chem. Ind. Ltd., Iriarai, Ota-ku, Tokyo). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1957, **60** (10), 1274-1277.—The decomposition of siloxanes with a mixture of NaOH and KOH in a sealed nickel crucible was studied. When fused at 210°, dimethylsiloxane oil, octaphenylcyclotetrasiloxane, diphenylsilanediol, siloxanes of the varnish type, and siloxanes modified with alkyl resins are quant. decomposed within 1, 2, 4, 4 and 4 hr., respectively. The products are either determined gravimetrically by the usual method or colorimetrically with ammonium molybdate at 400 m μ .

K. SAITO

3036. Paper chromatography of organomercury compounds. Jun Kanazawa, Kiyoshi Koyama, Masahiro Aya and Rokuro Sato (Agric. Chem. Inspection Sta., Kita-ku, Tokyo). *J. Agric. Chem. Soc. Japan*, 1957, **31** (12), 872-874.—An aq. soln. (0.001 ml) of organomercury compounds is spotted onto a filter-paper and chromatographed with *n*-butanol saturated with *N* aq. NH_3 soln., and the spots are detected with 1% diphenylcarbazone in ethanol. The R_F value increases with increasing number of carbon atoms in the organic radical (phenylmercury acetate, 0.39; phenylmercury chloride, 0.40; ethylmercury chloride, 0.27; methoxyethylmercury chloride, 0.18; methylmercury chloride, 0.17; at 30°); Hg^+ and Hg^{2+} remain at the initial position.

K. SAITO

3037. Quantitative analysis of terpenes by infra-red spectroscopy. III. Infra-red spectrophotometric determination of borneol and isborneol. Tsuneichi Takeshita and Masayoshi Kitajima (Res.

Lab., Japan Monopoly Co-op., Shinagawa-ku, Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (7), 993-999.—Pure borneol (**I**) and isborneol (**II**) were synthesised and their i.r. spectra measured in liquid paraffin. The absorption of the stretching vibration of free OH is stronger in **II** than in **I**, whilst that of associated OH shows a reverse trend. The *exo*-form (**II**) is subject to steric hindrance more marked than the *endo*-form (**I**), and shows less trend towards association. This difference is, however, only applicable to their qualitative analysis. **I** has characteristic absorption at 1103, 1054 and 1029 cm^{-1} , whereas that of **II** is at 1103, 1069 and 1000 cm^{-1} . Their determination in a binary mixture can be effected by the use of these five key-bands, Beer's law holding for <0.2 g per 10 ml in CS_2 . The error is $\approx 1\%$ (absolute) for both **I** and **II**.

K. SAITO

3038. Detection of pyridine and its derivatives. B. P. Lisboa (Tuberkulose-Forschungsinst., Borstel, Germany). *Naturwissenschaften*, 1957, **44** (23), 618-619.—At a pH of 7-2 in Sørensen's phosphate buffer, pyridine and its derivatives react with cyanogen bromide and a diamide (*e.g.*, barbiturates) to yield colours that are characteristic for several pyridine derivatives. By this reaction it is possible to distinguish the three pyridinemonomonocarboxylic acids, pyridine from α -picoline, and nicotinic acid from its esters. A table of colour values is presented.

E. KAWERAU

3039. Chromatographic identification of pyrazine bases. P. Dietrich and D. Mercier (Inst. de Biol. Phys.-chim., Paris). *J. Chromatography*, 1958, **1** (1), 67-69 (in French).—Homologous pyrazine bases have been satisfactorily separated by gas-liquid chromatography at 120°, with dinonyl phthalate as stationary phase, and 2-8 litres per hr. of *N* as carrier. Isomeric pyrazine bases were not satisfactorily separated. Methylated or other alkylated pyrazine bases, separated in groups by gas-phase chromatography, have been converted into pyrazinecarboxylic acids by oxidation with KMnO_4 , and separated by ascending chromatography on Whatman No. 1 paper for 15 hr. with *n*-butanol-formic acid-water (4:1:1). Spots were detected with 0.5% FeSO_4 soln. Spot-colours and R_F values are given for six pyrazinecarboxylic acids.

R. E. ESSERY

3040. Further studies with 2:4:7-trinitrofluorenone as a reagent for microscopic fusion analysis [of benzene and naphthalene derivatives]. D. E. Laskowski and W. C. McCrone (Illinois Inst. Technol., Chicago, U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 542-544.—These studies are an extension of previous work (*cf. Anal. Abstr.*, 1954, **1**, 6). Mixed fusion data are presented for 14 naphthalene derivatives and 11 benzene derivatives. The values of the significant m.p. are in most cases sufficient for identification of the compound tested. Most of the compounds of approximately the same initial m.p. may be differentiated by the colour of their 2:4:7-trinitrofluorenone addition compounds and the significant temp. as measured by the mixed fusion technique. Some benzene derivatives in mixed fusion behave similarly to polynuclear aromatics, and the high volatility of some members of this class renders identification difficult or impossible.

G. P. COOK

3041. Use of potentiometric titration for determining free alkali in solutions of phenols and aromatic sulphonic acids. M. A. Portnov and S. M. Shein (Filial of Inst. of Organic Intermediates and Dyestuffs). *Zavod. Lab.*, 1957, **23** (12), 1417-1420.—With antimony and saturated calomel electrodes the soln. is titrated potentiometrically with 0.5 N HCl to a pH of ≈ 5 . G. S. SMITH

3042. Applications of nitrometry. XIV. Utilization of diazo-coupling reaction. Masaharu Yamagishi, Makoto Yokoo and Saburo Inoue (Res. Lab., Takeda Pharm. Ind., Juso-nischinocho, Higashi-yodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1957, **77** (11), 1234-1236.—Phenol, 1- and 2-naphthol, 2-naphthylamine and barbituric acid ($< 500 \mu\text{g}$) are treated with an excess of diazobenzenesulphonic acid at pH 9 and the excess of acid is determined in a nitrometer with NaNO_2 soln. Sulphanilic acid (0.07% in N HCl) (1 ml) is diazotised with KNO_2 (0.42%, 0.1 ml) and coupled with the sample soln. (1 ml) in the presence of borax soln. (38% in 2 N NaOH) (0.5 ml). The excess of HNO_2 is decomposed with sulphamic acid (4% in 20% acetic acid) (0.5 ml) and dil. HCl (0.5 ml). The product is treated with NaNO_2 (2% in saturated aq. NaNO_2) (cf. *Anal. Abstr.*, 1956, **3**, 2149). The error is $< 1\%$. K. SAITO

3043. Determination of nitro compounds with titanium(III) - polyphosphate solution. (Application of polyphosphate to masking volumetric analysis.) Susumu Suzuki, Yoshihiro Muramoto, Morio Ueno and Teruzo Sugano (Inst. Chem., Kinki Univ., Fuse, Osaka, Japan). *Bull. Chem. Soc. Japan*, 1957, **30** (7), 775-778 (in English).—The determination of nitro compounds by reduction with excess of Ti^{3+} - polyphosphate and back-titration with a standard oxidising agent has been investigated. The reagent is made by dissolving 5 g of metallic Ti in 100 ml of hot conc. H_2PO_4 and adding the soln. to 1 litre of 0.1 N Na_2PO_4 ; it is standardised with KMnO_4 . The nitro compound (0.03 g) is dissolved in 5 ml of ethanol and heated under reflux in CO_2 for 5 min. with 25 ml of the reagent, before cooling and back-titrating in CO_2 with 0.1 N $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Ce}(\text{SO}_4)_2$ or NaVO_3 . Indicators are methylene blue, indigo carmine and diphenylamine; a known quantity of FeSO_4 must be used with the first and may be used with the others; the last gives a poor end-point with $\text{K}_2\text{Cr}_2\text{O}_7$ owing to formation of K_2CrO_4 . Of the 19 mono-, di- and tri-nitro compounds investigated, *o*-nitrophenol, *o*-nitroaniline and 4-nitrosalicylic acids gave the most accurate results (within $\pm 2\%$). A. B. DENSHAM

3044. Determination of *m*-nitrobenzoic acid in the electrolyte used for recovering tin from waste. N. N. Lapin and A. T. Slyusarev (Zhdanov Metallurgical Inst.). *Zavod. Lab.*, 1957, **23** (12), 1430-1432.—The method is designed for determining $\approx 2.5\%$ of *m*-nitrobenzoic acid in a 5% NaOH electrolyte when di-(3-carboxyphenyl)hydrazine is also present. It is based on the action of sodium stannite, which reduces only the former compound, in an atmosphere of H_2 . Into a flask, through which H_2 is flowing, are introduced 10 ml of 2 N NaOH, 1 or 2 ml of the electrolyte to be analysed and 15 ml of 0.1 N SnCl_2 in dil. HCl. After heating the mixture for 15 min. on a boiling-water bath, 20 ml of 2 N HCl and then water to give a vol. of 100 ml are added, and the soln. is titrated with iodine soln. in the presence of starch. The passage of H_2 is

continued until just before the titration. A blank is carried out to give the titre of the 0.1 N SnCl_2 . The theoretical factor for reduction of *m*-nitrobenzoic acid is used. G. S. SMITH

3045. Determination of the content of unsaturated hydrocarbons in crude benzene and benzene fractions. S. G. Faingol'd (Yasinov Chemical Coke Works). *Zavod. Lab.*, 1957, **23** (12), 1425-1426.—The sample (50 ml) is shaken for 15 min. with 10% of its vol. of 92 to 92.5% H_2SO_4 and then distilled into the burette originally used for measuring the sample, but now containing 10% NaOH soln. up to the zero mark. The loss, after allowance is made for the normal loss (0.8 to 0.9%) when pure benzene is used, corresponds to the amount of unsaturated hydrocarbons present. The distillation is continued until white fumes start to appear or a drop in temp. indicates the decomposition of polymers. G. S. SMITH

3046. Determination of tetraethyl-lead in motor spirits by flame photometry. W. Linné and H. D. Wülken (Hauptlab. Esso A.-G., Raffinerie, Hamburg). *Erdöl u. Kohle*, 1957, **10** (11), 757-758.—The flame emission of the sample is measured at 405.8 $\text{m}\mu$ (galvanometer deflection = *a*) and at 402.0 $\text{m}\mu$ (= *b*). A known vol. ($x\%$) of tetraethyl-lead (I) is added to the sample and the emission at 405.8 $\text{m}\mu$ is again measured (= *c*). Then the original content of I is $x(a-b)/(c-a)\%$ (v/v). The method depends on the fact that *b* corresponds with the variable background emission from the flame, so that no calibration curve or background correction is necessary. The precision is such that $3 \times$ standard deviation = $\pm 0.001\%$ (v/v) of I. In a series of analyses, each takes ≈ 5 min. A. R. PEARSON

3047. Argentimetric determination of tetraethyl-lead, dichloroethane and dibromoethane in anti-knock mixtures. G. Tagliarini (Inst. Gen. Chem., Padua Univ., Italy). *Chim. e Ind.*, 1957, **39** (11), 902-904.—To determine the tetraethyl-lead, the anti-knock fluid (0.1 to 0.2 g) is shaken with 1% AgNO_3 soln. (25 to 30 ml) in methanol at 80° . The resulting metallic silver is filtered off, dissolved in HNO_3 , and determined by the Volhard method. To determine the halides, the anti-knock fluid (0.5 to 1.0 g) is heated in a sealed tube at 130° to 140° for 1 hr., with butanol (40 ml) and Na (1.5 to 2.0 g). The resulting mixture is dissolved in 30% HNO_3 and the total halogen is determined by the Volhard method. Bromine is determined by potentiometric titration with 0.1 N AgNO_3 . Accuracies of $\pm 0.1\%$ are obtained. C. A. FINCH

3048. Determination of unsaturation in isopentane [2-methylbutane], isoprene and isoomylene [2-methyl-2-butene] mixtures by bromimetric methods. B. A. Kazanskiĭ, O. D. Sterligov, A. P. Belen'kaya, G. Ya. Kondrat'eva and P. S. Pavlova (N. D. Zelinskii Inst. Org. Chem., Acad. Sci., USSR). *Izv. Akad. Nauk, SSSR, Otdel. Khim. Nauk*, 1957, (11), 1399-1400.—Three known bromimetric methods for determining unsaturated compounds are compared. The methods of Rosenmund *et al.* (*Ber.*, 1923, **56**, 1262 and 2042) and Gal'pern (*Trudy Inst. Nefti, Akad. Nauk SSSR*, 1954, **4**, 116 and 140) are both applicable, but since the former gives a positive error and the latter a negative error in the analysis of mixtures containing 15% of isoprene it is necessary to apply correction factors, 0.96 and 1.04, respectively. G. S. SMITH

3049. Determination of iron in used lubricating oil. N. V. Mandryka and N. P. Kalutskaya ("Serp i molot" Works, Kharkov). *Zavod. Lab.*, 1957, **23** (12), 1430.—The sample (5 g) is dissolved in 50 ml of benzene and treated with 50 ml of dil. HCl (1:1) heated to between 60° and 70°. The mixture is stirred and poured into a separating funnel. The acid extract together with washings is used for a colorimetric determination of Fe. Results agree closely with those obtained by the ignition method.

G. S. SMITH

3050. Determination of copper in gelatin. G. Russell and P. J. Hart (Ilford Ltd., Woodman Rd., Brentwood, England). *Analyst*, 1958, **83**, 202-207.—Some newer methods for the determination of traces of Cu (up to 15 p.p.m.) have been applied to gelatin, and the results are compared with those of present procedures. Organic matter is destroyed by heating the sample (2 g) first with HNO₃, then with H₂SO₄, and finally with HClO₄, the excess of HClO₄ being then removed by prolonged heating. The diluted digest is treated with tartaric acid soln. and hydroxylamine soln., the pH is adjusted to between 4 and 7 with NaOH soln., pH paper being used as external indicator. After further dilution the liquid is maintained in a thermostatically controlled bath at 25° ± 0.5° for 10 min., 2:2'-diquinolyl soln. (0.2% w/v in purified isoamyl alcohol) is added and, after shaking, the organic layer is separated and its extinction is measured, an Ilford No. 625 filter being used, and referred to a calibration graph. Methods with biscyclohexanone oxalylidihydrazone and with 2:9-dimethyl-1:10-phenanthroline (neocuproin) as reagents are described, as well as a polarographic method. All are satisfactory, but for stated reasons the method with 2:2'-diquinolyl is preferred.

A. O. JONES

3051. Qualitative analysis of non-ionic surfactants on filter-paper. Toshio Nakagawa and Isami Nakata (Shionogi Pharm. Ind. Ltd., Imafuku, Amagasaki, Osaka). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1957, **60** (5), 554-556.—A benzene soln. of non-ionic surfactant is spotted on filter-paper, then developed with a mixture of *n*-butanol, pyridine and water (5 + 2 + 5) (cf. Nakagawa *et al.*, *Ibid.*, 1956, **59**, 1154) and treated with various reagents: modified Dragendorff's reagent or Co-thiocyanate complex (62 g of NH₄SCN and 22.8 g of CoCl₂·6H₂O in 100 ml of water) for polyoxyethylene groups, iodine-amylose for surfactants with a long-chain alkyl group, 0.4% KMnO₄ for those with a reductive group and conc. H₂SO₄ for resins. When combined with the periodate reagent test or hydrolysis with methanolic KOH, followed by neutralisation and extraction with benzene, this spot test enables eight main non-ionic surfactants to be readily differentiated and 31 others by careful measurements of the R_F value.

K. SAITO

3052. Qualitative and quantitative analysis of essential oils. I. Separation of constituents by paper chromatography. Sachio Kondo (Res. Lab., Sun Star Dentifrice Co. Ltd., Tatsumishijo, Ikunokuni, Osaka). *J. Pharm. Soc. Japan*, 1957, **77** (6), 694-696.—The use of polyethylene (I) for the treatment of filter-paper for paper chromatography was studied. The paper is impregnated with 1% I in toluene (60°) and dried at 90°. The R_F value is not markedly affected by the molecular wt. of I when the compounds (*e.g.*, anethole, coumarin, eugenol, heliotropin and cineole) are developed with methanol

containing 15% of isoamyl alcohol or 10% of benzene. This paper appears to be suitable for compounds without hydrophobic radicals.

K. SAITO

3053. Analysis of dyestuffs intermediates by infra-red absorption spectroscopy. I. Quantitative determination of isomers of chloronitrobenzene. Naofumi Oi and Kei-ichiro Miyazaki (Res. Dept., Osaka Works, Sumitomo Chem. Co., Kasugade, Konohana-ku). *J. Pharm. Soc. Japan*, 1957, **77** (9), 1027-1029.—Isomers of chloronitrobenzene are photometrically determined in 1% CS₂ soln. by the use of the bands at 12.94 (*o*-), 12.56 (*m*-) and 9.14 μ (*p*-) as key bands. The working curve is linear up to 6 mg each per ml. The standard deviations are ±0.63, ±0.33 and ±0.60% for the *o*-, *m*- and *p*-isomers, respectively.

II. Quantitative determination of chlorodinitrobenzene isomers. Naofumi Oi and Kei-ichiro Miyazaki. *Ibid.*, 1957, **77** (9), 1030-1032. Chloro-2:4-, -2:6- and -3:4-dinitrobenzene (the main components of chlorodinitrobenzene; the other isomers are negligible in amount) are determined by i.r. spectrophotometry in 1% CS₂ soln. with the bands at 9.55 (2:4-), 12.36 (2:6-) and 13.10 μ (3:4-) as key bands. The working curve is linear for <6 mg each per ml. The standard deviation is ±0.56% for the 2:4-, ±1.68% for the 2:6- and ±0.51% for the 3:4- isomer.

K. SAITO

3054. Amperometric titration of micro quantities of methylene blue and methyl violet with tungstosilicic acid. Tadahiko Ogawa (Fac. of Engng, Yokohama Univ., Minami-ku). *J. Electrochem. Soc. Japan*, 1957, **25** (12), 613-617.—Since methylene blue (I) and methyl violet (II) form insol. salts with tungstosilicic acid (III), an amperometric titration (at -0.70 V vs. the S.C.E.) of both dyes can be made in >N HCl with aq. III soln. (2.8 or 0.28 mg per ml). The pptn. proceeds rapidly at room temp. and a determination is completed within 40 min. with an average deviation of 2 to 3% for 0.05 to 4 mg of I and 0.08 to 6 mg of II. Substances that form insol. salts with III under the given conditions or that show a reduction wave at -0.70 V interfere.

K. SAITO

3055. Determination of the oxime-forming functions of degraded cellulose. J. Cyrot (Lab. de Chimie, Inst. Textile de France). *Chim. Anal.*, 1957, **39** (12), 449-453.—The carbonyl groups of oxidised cellulose are converted into oxime deriv. by treatment with 0.5 N hydroxylamine hydrochloride for 18 hr. at 30° and pH 6-8. The fibre is washed free from excess of reagent with water, washed with acetone, and dried at room temp., and N is determined by the Kjeldahl procedure of Grunbaum *et al.* (cf. *Brit. Abstr. C*, 1953, 87), without catalyst in a sealed tube at 460° ± 5°, for 2 to 3 hr., 30 min. being taken to reach this temp. The digest is made alkaline, 80 ml is distilled, 5 ml of Nessler reagent added, the mixture made up to 100 ml, allowed to stand for 5 min., and the extinction read at 430 mμ. Results are referred to a standard curve. The content of carbonyl groups in millimoles per 100 g of cellulose is given by 0.588 *a/b*, where *a* is the number of tenth-milligrams of NH₃ per 100 ml, and *b* is the weight (g) of oxidized cellulose taken. The method is applicable to cellulose only slightly degraded if the N in the unoxidized sample is allowed for. The periodate oxidation of cellulose is discussed.

R. E. ESSERY

3056. Analysis of black liquor from sulphate cooking of cellulose. B. Philipp and H. Hoyme (Inst. Textile Tech., German Acad. Sci., Berlin). *Faserforsch. u. Textiltech.*, 1957, **8** (9), 354-358.—In this rapid method (≈ 10 min.), the sulphide (I) is determined by direct titration with 0.1 M ZnSO_4 (II), with Eriochrome black T (III) as indicator. The NaOH and Na_2CO_3 are determined by pptg. I with the stoichiometric amount of II, and then making differential alkalimetric titrations of the product in the presence and absence of BaCl_2 . *Procedure*—For I, add a 2-ml sample to 150 ml of soln. containing 5 g of NH_4Cl and 5 ml of buffer (54 g of NH_4Cl and 350 ml of 25% aq. NH_3 per litre). A small amount of mixed indicator (III-methyl red - NaCl, 1:0.4:300) is added, and the soln. is titrated with II to a colour change from deep green to reddish brown. For NaOH and Na_2CO_3 , a 2-ml sample is diluted with ≈ 150 ml of CO_2 -free water, the stoichiometric amount of II is added, and the mixture is divided into two portions, to one of which is added 5 ml of 10% BaCl_2 soln. Both portions are titrated with 0.5 N HCl to phenolphthalein. H. L. WHITEHEAD

3057. Determination of viscose rayon and cotton in blend yarns and fabrics using sodium zincate solution. W. Armfield (Courtaulds Ltd., Droylsden, Manchester). *J. Text. Inst., Trans.*, 1957, **48** (12), T503-T505.—Viscose rayon is dissolved at 15° to 25° from spun mixtures of viscose rayon with raw, scoured or bleached cotton by a sodium zincate soln. which is 3 N with respect to NaOH and has a NaOH:ZnO ratio of 2.25 by wt. The method is not recommended for cotton which has a cuprammonium fluidity above 14. Results and errors are presented and discussed. O. M. WHITTON

3058. Tentative textile standard No. 48, 1957. Method for the quantitative chemical analysis of binary mixtures of polyamide fibres and certain other fibres. Textile Institute, Technical Committee. *J. Text. Inst., Proc.*, 1957, **48** (12), P782-P783.—Polyamide fibres are removed from their mixtures with cotton, viscose rayon and polyester fibres, and with wool (when the wool content of the mixture is $\geq 25\%$), by dissolving in 80% formic acid. The residue is collected, washed, dried and weighed; its wt. is corrected, when necessary, for loss in the solvent, and expressed as a percentage of the wt. of the mixture. O. M. WHITTON

3059. Tentative textile standard No. 49, 1957. Method for the quantitative chemical analysis of mixtures of viscose rayon and cotton. Textile Institute, Technical Committee. *J. Text. Inst., Proc.*, 1957, **48** (12), P784-P786.—The method is applicable, after the removal of added matter, to mixtures of viscose rayon with unscoured, scoured, kiered or bleached cotton. The cuprammonium fluidity of the cotton must not exceed 14. The viscose rayon is dissolved at room temp. (15° to 25°) from a known dry wt. of the mixture by means of a sodium zincate soln. The residue of cotton is collected, washed, dried and weighed; its wt. is corrected for loss in the solvent, and expressed as a percentage of the wt. of the mixture. The accuracy of the results is discussed. O. M. WHITTON

3060. Colorimetric determination of vinyl acetate in copolymers with vinyl cyanide. Yuzi Takayama and Shyohji Kadota (Mitsubishi Rayon Co., Kyobashi, Tokyo). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1957, **60** (9), 1159-1161.—Vinyl acetate

(I) (2 to 30%) in vinyl cyanide copolymers is saponified (90°, 2 hr.) with methanolic NaOH, esterified (3 hr.) with methanol and conc. H_2SO_4 , and converted into the hydroxamic acid, which is colorimetrically determined with FeCl_3 at 500 $\text{m}\mu$ (Takayama, *Anal. Abstr.*, 1956, **3**, 1082). The working curve is linear for < 10 mg of I. Poly(vinyl cyanide) turns brown on treatment with methanolic NaOH but remains undissolved. *Procedure*—Heat the sample (100 mg) with NaOH (2.5% in methanol) (0.5 ml) in an ampoule, then esterify with methanol (3 ml) and H_2SO_4 (0.2 ml). Extract three times with ether (total 30 ml) and mix a 1-ml portion with NaOH in methanol (2.5%, 1 ml) and hydroxylamine hydrochloride (2.5%, 1 ml) in ethanol. Set aside for 8 min. at 60° and for 5 min. at room temp., mix with FeCl_3 soln. (4 mg per 100 ml of ethanol) (*loc. cit.*) and measure the extinction at 500 $\text{m}\mu$ within 12 min. K. SAITO

3061. Semi-micro determination of chlorine in poly(vinyl chloride) and related polymers. J. Haslam and J. I. Hall (I.C.I. Ltd., Plastics Div., Welwyn Garden City, England). *Analyst*, 1958, **83**, 196-198.—The sample (20 mg), intimately mixed with 0.06 g of dried starch and 1 g of Na_2O_2 , is fired electrically in a specially constructed stainless-steel bomb, which is then cooled by immersion in water. The melt is dissolved in water, the soln. is boiled, cooled, and adjusted to a stated degree of acidity with HNO_3 . The Cl^- are titrated with 0.02 N AgNO_3 by means of the automatic titrimeter (Haslam *et al.*, *Analyst*, 1954, **79**, 689; 1957, **82**, 511). The pre-set end-point is determined by titrating 0.02 N NaCl by an initial manual titration in the titrimeter. The 0.02 N AgNO_3 is standardised against NaCl that has been fused with Na_2O_2 in the same manner as the sample, and a reagent blank determination is made. Results agree satisfactorily with those found by the Carius method, and the method can be used to determine Cl in copolymers containing N. A. O. JONES

3062. Analysis of epoxy resins. E. Gulinsky and H. Gruber. *Felle, Seif., Anstrichmitt.*, 1957, **59** (12), 1093-1095.—Known methods for the analysis of epoxy resins are discussed. These include the qual. determination of epoxy resins, the determination of epoxy, hydroxyl and ester values, and the determination of the epoxy-resin content of lacquer-binding materials and paint films. E. HAYES

3063. Determination of acid amides in methyl methacrylate processing. Tsugio Takeuchi, Motohisa Furusawa and Yuzi Takayama (Fac. of Engng, Yamanashi Univ., Motoyanagi-cho, Kofu). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1957, **60** (11), 1448-1451.—Nitrogen both in the amino and ammonium form in an intermediate for the preparation of methyl methacrylate is distilled as NH_3 in the presence of NaOH; acetone cyanohydrin (< 0.1 g) does not cause interference in the presence of FeSO_4 . The amount of ammonium N is determined volumetrically in the presence of formaldehyde and deducted from the result. Neither methacrylic acid nor its methyl ester gives a significant error. *Procedure*—Mix the sample soln. (containing N equiv. to ≈ 20 ml of 0.1 N H_2SO_4) (20 ml) in aq. methanol with FeSO_4 (5%, in 0.1 N H_2SO_4) (20 ml), dilute to 100 ml and distil with 5 N NaOH (100 ml) into 0.1 N H_2SO_4 (25 ml) until 50 ml of distillate is collected. Titrate the distillate with 0.1 N NaOH (to methyl red). Neutralise the

sample soln. with N NaOH (to methyl red) and dilute to 70 ml with 0.1 N H_2SO_4 (5 ml) and water. Boil for 10 min., neutralise with 0.1 N NaOH, and carry out the usual formaldehyde titration.

K. SAITO

3064. Determination of foots in raw linseed oil. P. J. de Coninck and J. Delacourt (Raffineries du Congo Belge, Baasrode). *Olii Min.*, 1957, **34** (9), 409-419.—*Cf. Chim. Peint.*, 1956, **19**, 445; *Anal. Abstr.*, 1958, **5**, 266.

E. C. APLING

3065. Analysis and evaluation of polishes. L. Ivanovsky (Borough Polytechnic, London). *Paint Manuf.*, 1957, **27**, 433-435, 440.—A general scheme is outlined. The total residue is determined, preferably in a vacuum oven; water and alcohol-soluble components of the residue are extracted and insol. inorg. matter is separated by filtration after treatment with hot solvents. Silicone fluids can usually be recognised by the formation of an "eye" on the surface of the solidified residue. Org. matter is examined by determination of appropriate constants and use of special tests. Volatile components are examined after steam-distillation. The main raw materials used for 22 types of polish are shown in tabular form.

L. A. O'NEILL

3066. Methods of testing vulcanised rubber. Parts B6 to B10. Determination of sulphur. British Standards Institution (2 Park St., London). B.S. 903: Parts B6 to B10: 1958, 25 pp. This Standard is a replacement of B.S. 903: Part 3: 1950.—*Total sulphur*—The Carius and fusion methods are unaltered from B.S. 903: Part 3: 1950 except for deletion of the optional use of picric acid before pptn. of $BaSO_4$. A re-designed absorption vessel is specified for the combustion method, and the titrimetric finish is modified to cover samples containing vinyl cyanide-type polymers and/or chlorine-containing compounds. *Extractable sulphur*—The bromine and nitric acid methods are unaltered from B.S. 903: Part 3: 1950, except for deletion of the optional use of picric acid before pptn. of $BaSO_4$. An all-glass Quickfit apparatus is specified for the copper-spiral method and the concn. of the $Na_2S_2O_8$ and iodine soln. are 0.05 N instead of 0.1 N . The rest of the method is the same as in B.S. 903: Part 3: 1950. *Rubber-combined sulphur*—The same as in B.S. 903: Part 3: 1950. *Sulphur in "total fillers"*—The method is unaltered from B.S. 903: Part 3: 1950, except for deletion of the optional use of picric acid before pptn. of $BaSO_4$. *Sulphide sulphur*—The all-glass apparatus specified for the extractable sulphur procedure is also specified for this method and the $Na_2S_2O_8$ and iodine soln. are also 0.05 N instead of 0.1 N . The rest of the method is the same as in B.S. 903: Part 3: 1950.

G. H. FOXLEY

3067. Comparison of the results of estimating black wattle tannin by the official hide-powder method and by a proposed ultra-violet spectrophotometric method. C. G. Gordon-Gray (Wattle Res. Inst., Univ. of Natal, Pietermaritzburg, S. Africa). *J. Soc. Leath. Tr. Chem.*, 1957, **41** (8), 269-275.—The u.v. spectrophotometric method of Roux (*cf. Brit. Abstr. C*, 1953, 18; 1952, 155) has been compared with the official hide-powder method, with 94 black, 3 green, and 19 silver wattle barks. For the former method, the bisulphite soln. should be made up afresh for each set of determinations, and the readings corrected for the change in extinction with time of the standard benzoic acid soln. All

spectrophotometers should be calibrated with the same parent extract, which is standardised by the hide-powder method in duplicate by a single analyst; barks should be ground to a homogeneous powder, their moisture contents accurately determined, extracts made by the Koch or Procter methods, and opalescence in the extracts, as diluted for reading, accepted. With these precautions, reproducibility of the u.v. method was good, and agreement between different instruments excellent. Differences between methods of <1% were obtained with 60 black, 1 green and 1 silver bark; differences were seldom >3% with black barks, but might be up to 6% with silver barks. Good agreement between laboratories was obtained by both methods. The differences did not bear any constant relation to the official method, and, although the u.v. measurement is rapid, the necessity for a Procter extraction imposes a limit on the speed of analysis.

R. E. ESSERY

3068. Estimation of tannins in black wattle barks and commercial "mimosa" extracts. II. Statistical comparison of the official hide-powder (shake) method and photometric methods of tannin analysis. D. G. Roux (Leather Ind. Res. Inst., Rhodes Univ., Grahamstown, S. Africa). *J. Soc. Leath. Tr. Chem.*, 1957, **41** (8), 275-286.—The results of Gordon-Gray (*cf. Anal. Abstr.*, 1958, **5**, 3067) are analysed statistically. It is shown that the agreement between methods is high (correlation coefficient $r = 0.961$ and standard deviation of the differences $s = \pm 1.34$), but individual differences up to 4% are found, which are ascribed mainly to inherent differences between methods, with experimental error contributing a minor but appreciable proportion. That both methods reflect the same tannin content is further shown by the regression lines for each method, both of which lie close to the 45° equivalence line. Results for the two methods with commercial extracts gave $r = 0.977$ and $s = \pm 0.63$. This improved agreement is probably due to the fact that commercial extracts represent the pooled extractives from a large number of barks, and that mixing of green and dried barks during manufacture ensures uniformity of product. Some analyses by the ferrous tartrate method of Roux (*cf. Brit. Abstr. C*, 1952, 155) showed good agreement with the hide-powder method for extracts and bark, but wide divergence with spent bark. It is concluded that the adoption of the u.v. method as an alternative will have no serious commercial implications.

III. A critical examination of the official hide-powder method. D. G. Roux. *Ibid.*, 1957, **41** (8), 287-300.—Commercial black wattle extracts contain three main groups of components, polyphenols ($\approx 60\%$), sugars ($\approx 10\%$) and gums (5 to 12%). After a discussion of the deficiencies in hide-powder methods, in relation to the material being analysed and to tannery results, the behaviour of these three groups towards hide-powder is examined under the conditions of the official test. It is shown that the hide-powder method enables 4 to 6% of the polyphenol fraction to escape, which is, however, absorbed by hides during tanning; 55 to 81% of the gums react as tannins towards hide-powder under standard conditions, although in actual tanning 55% of the gums play no part in the process. Sugars are returned as non-tans by the hide-powder process, although they are partially "absorbed" by hides during tanning. Of the photometric processes of Roux (*cf. Brit. Abstr. C*, 1952, 155), the ferrous tartrate method measures the α -hydroxyphenolic function of the tannins, and the u.v. method the

total phenolic function. Neither method is affected by sugars, gums or starch. A compensation of errors in the hide-powder method, and the fact that the u.v. method is standardised against hide-powder probably accounts for the high correlation between the methods (*cf.* Part II, above). The significance of these findings in relation to tannery practice and the analysis of other vegetable extracts is discussed, and it is noted that the assessment by the hide-powder method of the true tannin content of the latter requires that the composition and nature of the extract be known. Photometric methods are rapid and differentiate better than hide-powder methods between tannins and non-tannins. The high cost of the apparatus is offset by the high cost of hide-powder and the saving of time.

R. E. ESSERY

3069. Infra-red quantitative analysis data. *Anal. Chem.*, 1958, **30** (4, Part I), 549-550.—The following data have been published under the co-operative programme between *Analytical Chemistry* and the Coblentz Society of the U.S.A. **Determination of water in liquid bromine**, R. B. Duvall and L. R. Kiley. **Determination of naphthalene in cracked 1-methylnaphthalene**, S. Drexler. **Quantitative determination of methoxy groups in siloxane polymers**, P. Brown and A. Lee Smith. **Determination of cumene and α -methylstyrene in crude α -methylstyrene**, J. V. Hopson. **Determination of *p*-xylene, *m*-xylene and *o*-xylene in xylene mixtures**, D. M. Frankel and C. E. Johnson. **Determination of 2-ethyl-1-methylbenzene, 3-ethyl-1-methylbenzene, and 4-ethyl-1-methylbenzene**, J. G. Ehlers. **Analysis of 3:5-dimethylpyridine, 2:3:6-trimethylpyridine, and 2:4:6-trimethylpyridine mixtures**, D. D. Shrewsbury.

3070. Infra-red spectra of oxirane compounds. Correlations with structure. J. Bomstein (Food Machinery and Chem. Corp., Buffalo, N.Y., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 544-546.—The spectra (2 to 15 μ) of 11 oxirane compounds (mainly non-terminal epoxides) are listed. The 12- μ band is most sensitive to structural changes. Several very intense 11- and 12- μ bands are suitable for routine i.r. quant. analyses. Tri-substituted rings have a band at 13.0 to 13.3 μ , di-substituted rings a band at 11.8 to 12.9 μ , and mono-substituted rings a band at 11.4 to 12.4 μ . Oxirane rings form complexes with iodine.

W. J. BAKER

See also Abstracts—3176. Detection and determination of chlorinated ethylenic solvents in air. **3207.** Use of mixed stationary liquids in gas-liquid chromatography. **3208.** A sensitive detector for gas chromatography. **3210.** Calculator for use in organic chemical analysis. **3220.** Portable interferometer for fire-damp detection. **3222.** Carbon and hydrogen combustion train.

4.—BIOCHEMISTRY

INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

3071. Improved procedure for preparation of tissues for chemical analyses. L. Eichelberger and J. S. Miles (Dept. of Surgery and Biochemistry, Univ. of Chicago). *Proc. Soc. Exp. Biol. Med.*, 1956, **93**, 584.—Procedures are described for pro-

ducing homogeneous preparations. Remove the tissues from anaesthetised animals, cool them in a refrigerator, then trim and cut them up with scissors. Weigh in Vycor crucibles at room temperature, heat at 100° for 48 hr. in an oven, cool in a desiccator over activated alumina and weigh. Cover with dry diethyl ether and place for 24 hr. in another desiccator containing ether to remove fat. Repeat three times. Heat in an oven for 5 hr., dry over alumina and weigh the fat-free solid. Grind for analyses in a Zassenhaus spice or pepper mill and keep in a sealed jar. Finer samples are ground in a mullite mortar.

G. F. SOMERS

3072. Bloodless determination of arterial-oxygen tension by polarography. G. Rooth, S. Sjöstedt and F. Caligara (Univ. Hosp., Lund, Sweden). *Sci. Tools*, 1957, **4** (3), 37-42.—A modification of Baumberger's method is described. A cleaned finger of the subject is immersed for ≈ 15 min. in a Plexiglas cell containing 3 to 5 ml of 0.8 N aq. KCl, pre-saturated with O and N to pO_2 (oxygen tension) = 70 mm (Hg) and kept at a const. temp. of 45-2°. The pO_2 of the KCl soln. (in equilibrium with that of the arterial blood) is then measured polarographically with platinum and silver-silver chloride electrodes from 0 to -0.8 V. The oxygen wave recorded on the polarogram is converted into the corresponding pO_2 value by reference to a calibration curve for standard soln. [pO_2 = 70 to 105 mm (Hg)]. The result is unaffected by the pre-wave (0.5 to 1.1 μA) caused by unknown substances. The results conform with those given in the literature.

W. J. BAKER

3073. Estimation of calcium in urine by flame photometry, with a note on the estimation of sodium and potassium. W. P. U. Jackson and L. Irwin (Dept. of Med., Univ. of Cape Town, S. Africa). *J. Clin. Path.*, 1957, **10** (4), 383-386.—Urine is acidified with conc. HCl (1 ml to 100 ml of urine) and filtered. The filtrate (10 ml) is passed through a column (12.5 cm \times 6 cm) of Dowex 50, 50 to 100 mesh, and the resin is washed with H_2O (2 \times 10 ml). The Na^+ and K^+ are eluted with N HCl, exactly 20 ml of eluate being collected, and the Ca^{++} are then eluted with 3 N HCl, 35 ml of eluate being collected. The determinations are made with a Beckman spectrophotometer, with flame and photomultiplier attachments.

H. F. W. KIRKPATRICK

3074. New dye method for direct photometric determination of calcium [in serum]. G. R. Kingsley and O. Robnett (Veterans Admin. Center, Los Angeles, Calif., U.S.A.). *Amer. J. Clin. Path.*, 1957, **27**, 223-230.—A method is based on the red colour which disodium 5-chloro-2-hydroxyazo-benzene-1:8-dihydroxynaphthalene-3:6-disulphonate (Plasmocorinth B) gives with Ca. In the prevailing alkaline conditions, Mg in serum does not interfere.

NUTR. ABSTR.

3075. Micro-determination of serum calcium using the EEL flame photometer. E. C. Butterworth (N. Staffs. Royal Infirmary, Stoke-on-Trent, England). *J. Clin. Path.*, 1957, **10** (4), 379-382.—Calcium is pptd. from serum (0.2 ml) with saturated aq. ammonium oxalate soln. (0.4 ml) and set aside for 30 min. After centrifuging and draining, the ppt. is dissolved in hot 0.5 N H_2SO_4 (1 ml), cooled, and 10% (v/v) *n*-propanol (2 ml) is added. The

soln. is sprayed from 5-ml beakers with an air pressure of 15 lb per sq. in. to increase sensitivity.

H. F. W. KIRKPATRICK

3076. Complexometric titration of urinary calcium and magnesium. C. L. Yarbro and R. L. Golby (Univ. North Carolina, Chapel Hill, U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 504-506.—Urinary Ca is determined by addition of an excess of standard 1:2-di-(2-aminoethoxy)ethane- NN' -tetra-acetic acid and back-titrating with Ca^{2+} , with Calcon as indicator. Total Ca plus Mg is determined by addition of an excess of EDTA (disodium salt), followed by back-titration with Ca^{2+} , Eriochrome black T being used as indicator. Phosphate and citrate normally present in urine do not interfere. Protein in concn. >1 mg per ml interferes, but may be removed by pptn. with trichloroacetic acid. The recovery of Ca added to urine ranged from 38 to 104%, and of Mg from 35 to 105%. Twenty triplicate titrations of urinary Ca agreed within $\pm 2.9\%$ over the concn. range of 2.23 to 8.94 millimoles per litre. Twenty aliquots of one urine sample gave the following results— $\text{Ca} = 8.41 \pm 0.032$, $\text{Mg} = 6.03 \pm 0.177$ millimoles per litre.

G. P. COOK

3077. Use of EDTA (disodium salt) in determinations of barium in biological material. A. N. Krýlova. *Apteknoe Delo*, 1957, **6** (6), 28-32.—In the determination of Ba^{2+} in biological materials by pptn. as BaSO_4 , results can be up to 144% high; this is due to co-pptn. of other salts, mainly those of Ca and Pb. If the BaSO_4 is re-pptd. from an ammoniacal soln. of EDTA (disodium salt), Fe is completely removed and the content of calcium salts is reduced to between 6 and 8%. Attempts to determine Ba^{2+} complexometrically were not successful; the method of Belcher *et al.* (*Anal. Abstr.*, 1954, **1**, 448) gives erratic results in determinations on biological materials.

E. HAYES

3078. Butanol-extractable iodine of serum determined by dry-ashing procedure. Soichi Kumaoka and Yoshio Tobo (Dept. of Intern. Med., Niigata Univ. Sch. of Med., Japan). *Acta Med. Biol.*, 1957, **5** (3), 201-207 (in English).—Serum (1 ml) is acidified with 10% H_2SO_4 (2 drops) and extracted by shaking and centrifuging with *n*-butanol (5 ml + 4 ml + 3 ml). The combined extracts are washed 3 times with an equal vol. of 4 *N* NaOH containing 5% of Na_2CO_3 . The butanol is evaporated, the residue is dissolved in 0.05 *N* NaOH (1 ml), 10% ZnSO_4 soln. (1 ml) is added and the tube is placed obliquely in an oven at 90° overnight to dry completely. The residue is ashed at $480^\circ \pm 5^\circ$ for 30 min., the ash is dissolved in 2 *N* HCl (2 ml), then 7 *N* H_2SO_4 (2 ml) and H_2O (3 ml) are added and the soln. is mixed and centrifuged at 3500 r.p.m. for 15 min. The determination is completed on 3 ml of supernatant fluid, as described by Barker (*J. Clin. Endocrin.*, 1950, **10**, 1136).

H. F. W. KIRKPATRICK

3079. Determination of urinary excretion of radio-cobalt-labelled vitamin B_{12} by cobalt sulphide precipitation. D. S. Kinnor, E. Kaplan, Y. T. Oester and A. A. Imperato (Veterans Admin. Hosp., Hines, Ill., U.S.A.). *J. Lab. Clin. Med.*, 1957, **50** (6), 913-917.—A tracer dose of 0.05 μC of ^{60}Co -labelled vitamin B_{12} given orally is followed after 1 hr. by intramuscular injection of 1 mg of non-radioactive vitamin B_{12} . The total urine during the following 24 hr. is collected, CoCl_2 is added as

carrier, and Co is pptd. with $(\text{NH}_4)_2\text{S}$ in the presence of NH_4Cl . The CoS is collected on glass-fibre filter-paper and counted in a small tube placed in a well-type scintillation counter. The method has the advantages of small dosage with radioactive material and avoidance of interference by radio-isotopes not pptd. by $(\text{NH}_4)_2\text{S}$.

W. H. C. SHAW

3080. Micro-determination of thallium in biological media by enrichment and polarography. R. Truhaut and C. Boudène. *Bull. Soc. Chim. France*, 1957, (11-12), 1504-1507.—Thallium is determined in urine and blood by mineralisation and pptn. as iodide entrained by Pb. The ppt. is dissolved in EDTA (disodium salt) soln., which suppresses the Pb wave, and is polarographed. *Procedure*—Urine (5 to 30 ml) is added to 800 μg of Pb and 5 ml of HNO_3 and evaporated down to a whitish residue. Blood (2 to 10 ml) is added to 800 μg of Pb and treated with successive amounts of HNO_3 -100-vol. H_2O_2 . The residue, after evaporation with 0.5 ml of conc. HCl, is boiled with 4 ml of hydroxylamine hydrochloride soln. (10%) and, after it has dissolved, 4 ml of acetate buffer is added. A soln. of KI (30% containing a little sulphite) (2 ml) is added to the soln. in a centrifuge tube, followed by $\text{Pb}(\text{NO}_3)_2$ (2 mg per ml) until a permanent ppt. is formed. The ppt. is centrifuged and evaporated to dryness with HNO_3 -100-vol. H_2O_2 . The residue is evaporated with H_2O , then treated with 0.5 ml of hydroxylamine hydrochloride soln., and evaporated to half its vol. EDTA (disodium salt) is added (0.5 ml of 6% aq. soln.) with 0.8 ml of acetate buffer and 0.2 ml of urea soln. (10%). The soln. (pH 4.0 to 4.5) is deoxygenated and polarographed; $E_1 = \approx -0.43$ V. The Pb does not interfere in the presence of EDTA and Bi does not interfere as it has been transformed into alkali iodobismuthite.

E. J. H. BIRCH

3081. Chemical determination of digitoxin in tissues and excreta. K. Repke (Inst. Med. Biol., Dtsch. Akad. d. Wissch., Berlin, Germany). *Naturwissenschaften*, 1957, **44** (23), 619-620.—The homogenised material is extracted twice with CHCl_3 and fractionated and purified on alumina columns. The quant. determination is then carried out either by the xanthhydrol reaction of Pesze (*cf. Brit. Abstr. C*, 1952, 452) or by the author's new procedure with *m*-dinitrobenzene (to be published in full later). The recovery of added digitoxin is $>90\%$ by both methods. The lower limit of detection for the xanthhydrol method is $\approx 0.1 \mu\text{g}$ of digitoxin.

E. KAWERAU

3082. A cylinder test for the quantitative determination of tetracycline and its derivatives in body fluids. T. Dimmling (Inst. for Hyg. and Microbiol., Univ. of Würzburg). *Arzneimittel-Forsch.*, 1957, **7** (11), 684-686.—Tetracycline (I), oxytetracycline (II) and chlortetracycline (III) in serum, urine, cerebrospinal fluid, etc., are determined by comparing the zone of inhibition of a spore suspension of *Bacillus cereus* var. *mycoides* P.C.I. 213 round small steel cylinders containing samples of the serum, etc., with that round control cylinders containing known concn. of the antibiotic. The method enables $\approx 0.05 \mu\text{g}$ of I and II per ml and 0.01 μg of III per ml to be determined.

A. COOPER

3083. Rapid oscillopolarographic method for the detection and semi-quantitative determination of barbiturates in biological materials. F. Vorel and J. Prokeš (Lab. of Toxicol., Charles' Univ., Prague).

Soudní Lékařství, 1957, **2** (9), 129-132.—The method is based on extraction of the barbiturates with ether from acid soln. and separation of impurities and inhibiting substances by means of ascending chromatography on Whatman No. 3 paper in acetone. Barbiturates are detected in the eluate by oscillography, the incision in the cathodic part of the oscillogram being compared with a standard. The error is $\pm 10\%$. The whole analysis does not take more than 1.5 hr. The method is suitable for chemi-forensic and clinical purposes.

J. ŽYKA

3084. Estimation of BZ55 [carbutamide] and sulphonamides in blood-sugar filtrates. D. G. Moss (Withington Hosp., Manchester). *J. Clin. Path.*, 1957, **10** (4), 371-372.—Wash capillary blood (0.2 ml) into isotonic Na_2SO_4 - CuSO_4 soln. (3.5 ml), add 10% sodium tungstate soln. (0.3 ml) and centrifuge. To the filtrate (1 ml) add N HCl (0.2 ml) and 0.1% NaNO_2 soln. (0.1 ml), mix well and add 1.8% aq. *N*-sulphatoethyl-*m*-toluidine soln. (2 ml). Read the orange colour at 495 μm . Prepare a standard with 0.015% sulphonamide soln. (1 ml) treated as the filtrate. If the blood sugar is not required, a filtrate prepared by zinc hydroxide pptn. of proteins may be used.

H. F. W. KIRKPATRICK

3085. Estimation of the oral hypoglycaemic agent carbutamide in blood. R. H. Thompson (Royal Victoria Hosp., Belfast, N. Ireland). *J. Clin. Path.*, 1957, **10** (4), 369-370.—A modification of the Bratton and Marshall method is used. To water (7.9 ml) add blood (0.1 ml), mix and add 15% trichloroacetic acid (2 ml), mix and centrifuge. To the filtrate (5 ml) add 0.1% NaNO_2 soln. (0.5 ml) and set aside for 3 min. Add 0.5% ammonium sulphamate (0.5 ml) followed, after 2 min., by 0.5% *N*-1-naphthylethylenediamine soln. (1 ml). Read the extinction after 15 min. at 540 μm . A blank and a standard soln. (5 ml) containing 1 μg of carbutamide per ml are treated similarly.

H. F. W. KIRKPATRICK

3086. Quantitative determination of carbohydrates by descending paper chromatography. G. N. Zaitseva and T. P. Afanas'eva (Fac. of Biol. and Soil Sci., Moscow State Univ.). *Biokhimiya*, 1957, **22** (6), 1035-1042.—With sufficient polysaccharide hydrolysate to give $<500 \mu\text{g}$ of sugars, based on their reducing ability, carry out the partition on a double strip of paper, with benzene-*n*-butanol-pyridine-water (1:5:3:3) as solvent, which separates uronic acids, glucosamine, galactose, glucose, mannose, xylose, ribose and rhamnose; the solvent is passed three times, for 24 hr. each. This solvent does not separate mannose, arabinose and fructose; for this separation use phenol-butanol-acetic acid-water (5:5:2:10), passed three times for 72 hr. each. Dry the chromatogram, cut it in half and develop one half with aniline phthalate and estimate the sugars in the spots. With the developed strip as a guide, cut out the sugar spots from the other half of the chromatogram, extract with water and determine the sugars separately. The following methods of determination are described, and standard curves given when appropriate (the sensitivities and error in brackets)—the aniline phthalate method (30 to 200 μg); the iodimetric method (30 to 350 μg , $\pm 2\%$); the anthrone method (10 to 100 μg , $\pm 5\%$); the orcinol method (5 to 40 μg for pentoses, 15 to 80 μg for methylpentoses, $\pm 3\%$); Kulka's method for keto

sugars (5 to 80 μg , $\pm 1\%$); and the phenol method (4 to 40 μg , $\pm 5\%$). Of these methods the simplest but least sensitive is the aniline phthalate method, which does not require careful removal of traces of solvents and shreds of paper, as do the others. The methods are used in analysing the hydrolysate of the polysaccharides of *Azotobacter agilis*, and give comparable results.

C. D. KOPKIN

3087. Rapid colorimetric micro-method for estimating glucose in blood and c.s.f. using glucose oxidase. J. E. Middleton and W. J. Griffiths (St. Thomas's Hosp., London). *Brit. Med. J.*, 1957, 1525-1527.—Blood (0.2 ml) is deproteinised with ZnSO_4 - NaOH and an aliquot of the filtrate is added to a buffered glucose oxidase soln. containing *o*-toluidine. The blue colour which develops is read, after setting aside the soln. for 10 min. at room temp., at 680 μm against a blank, and the reading is referred to a standard graph. Cerebrospinal fluid (0.4 ml) is treated similarly. The normal range of fasting blood sugar by this method is 50 to 90 mg per 100 ml.

H. F. W. KIRKPATRICK

3088. Determination of inulin in blood and urine using glucose oxidase for the removal of interfering glucose. E. R. Froesch, J. B. Reardon and A. E. Renold (Harvard Med. Sch., Boston, Mass., U.S.A.). *J. Lab. Clin. Med.*, 1957, **50** (6), 918-921.—The method is suitable for samples containing high proportions of glucose which is oxidised to gluconic acid in the presence of purified glucose oxidase. Inulin is then determined by the resorcinol method of Higashi and Peters (*J. Lab. Clin. Med.*, 1950, **35**, 475) in which gluconic acid does not interfere. Blank values on normal urine were $<3.25 \text{ mg}$ and averaged 0.75 $\text{mg} \%$; the recovery of added inulin is quantitative.

W. H. C. SHAW

3089. Identification of the organic acids in human plasma by paper chromatography. R. Nordmann, A. Marty, A. Tholozan and J. Nordmann (Clinique Chirurg. de la Salpêtrière, Paris). *Compt. Rend.*, 1957, **245** (25), 2414-2417.—The procedure permits simultaneous detection of 20 or more organic acids (except the most volatile) in plasma from normal fasting subjects. The sample (8 ml), adjusted to pH 5.3 with acetic acid, is deproteinised by heating and filtration. The filtrate is passed through a column of the formate form of Dowex 2X-10 resin (40 mm \times 4 mm, 60 to 80 mesh) and the organic acids are then eluted with 12 *N* formic acid (10 ml). The eluate is concentrated at 40° and is then chromatographed in two directions on Whatman No. 1 paper with the same acid and alkaline solvent phases used previously (Nordmann *et al.*, *Anal. Abstr.*, 1954, **1**, 3052). The developing reagents for revealing spots of the following acids are listed—lactic, citric, malic, succinic, acetic, α -oxoglutaric, tartaric, pyrrolidonecarboxylic, hippuric, *m*- and *o*-hydroxyhippuric, uric, oxalic, H_2PO_4 , H_2SO_4 , HCl , *p*-hydroxyphenylacetic and 2-*m*-hydroxyphenylhydracrylic. The identity of the two last-named acids is not yet certain.

W. J. BAKER

3090. Colorimetric determination of glucuronic acid. Hidenobu Kawabata, Suichi Tomioka and Kan Umeno (Technical Dev., Chûgai Pharm. Co., Takada-minamicho, Toshima-ku, Tokyo). *J. Pharm. Soc. Japan*, 1957, **77** (7), 767-770.—Modification of Foulger's method (*J. Biol. Chem.*, 1932,

99, 207) for the analysis of glucuronic acid preparations was studied. The extinction coeff. increases with increase in concn. of H_2SO_4 (20 to 50%) and with decrease in concn. of urea (10 to 40%). The working curve is linear for 0.05 to 0.3% of glucuronolactone. Fructose, rhamnose, maltose, glucose, lactose, arabinose, galactose and xylose do not cause interference (error <3% in the presence of 0.1 g of each). An aq. soln. of the sample ($\approx 0.1\%$, 1 ml) is mixed with urea soln. (10%, in 40% H_2SO_4) (10 ml), heated in a boiling-water bath, cooled for 1 min. with ice, and set aside for 10 min. The extinction is measured at 440 $m\mu$. K. SAITO

3091. Detection of α -keto-oxo-glutaric acid and other keto acids on paper chromatograms with ninhydrin. R. Rabson and N. E. Tolbert (Biology Div., Oak Ridge National Lab., Tenn., U.S.A.). *Nature*, 1958, **181**, 50-51.—Two-dimensional paper chromatograms of soluble plant extracts or known keto acids, with water-saturated phenol as first solvent and *n*-butanol-propionic acid-water as the second (cf. Benson *et al.*, *Brit. Abstr. C*, 1950, 417), are dried and sprayed with 0.1% ninhydrin in 95% ethanol containing 2 drops of 2:6-lutidine per 100 ml. After being heated at 90° for 3 to 5 min. and stored for at least 24 hr. in the dark, the papers are examined in light of 366 $m\mu$. α -Oxoglutaric acid gives an intense yellow fluorescence, <1 μg being easily detected. Pyruvic, α -oxobutyric, 2-oxo-gluconic and oxalacetic acids also gave fluorescent reactions, but glyoxylic acid did not. No β -keto acid reacted, nor did citric, malic, fumaric, lactic, glyceric, succinic or glycollic acid. The colours in white light were too weak to be useful. In various degrees, collidine, the picolines and pyridine could replace lutidine, but not NaOH or Na acetate. Hydrindantin and alloxan were not satisfactory as replacements for ninhydrin, while indane-1:3-dione gave a yellow spot with α -oxoglutaric acid which did not fluoresce in u.v. light. R. E. ESSERY

3092. Estimation of physiologically active, naturally occurring substances in the tissues and body fluids: acetylcholine, (-)-adrenaline, (-)-noradrenaline, histamine, serotonin and Substance P. V. [Histamine]. J. J. Lewis and N. G. Watson (Dept. of Mat. Med., Univ., Glasgow, Scotland). *Lab. Practice*, 1957, **6** (12), 707-711.—Current methods for the separation (adsorption and cation exchange) and determination by biological assay of histamine are reviewed. The method in which the contraction of guinea-pig ileum is used is described in detail. E. J. H. BIRCH

3093. Determination of amino acids by a radioisotope dilution method combined with paper chromatography. II. Amino-acid content of protein. Tsuru Wada (Inst. of Applied Microbiology, Tokyo Univ., Hongo). *J. Agric. Chem. Soc. Japan*, 1957, **31** (10), 743-748.—The method previously described (cf. *Anal. Abstr.*, 1957, **4**, 2324) was applied to the determination of glutamic acid, aspartic acid, glycine, alanine, valine, leucine (or isoleucine), lysine and arginine in Taka-amylase, ovalbumin and whale insulin. The sample, hydrolysed with 6 *N* HCl, is mixed with standard amino acids containing a known amount of ^{14}C and subjected to electrophoresis to separate the amino acids into acidic, neutral and basic groups. Each is submitted to paper chromatography with a mixture of butanol and aq. NH_3 soln. The overall error is <3% (absolute). K. SAITO

3094. Chromatographic determination of glutamic, aspartic and cysteic acids using an anion-exchange resin. A. M. Marko (Dept. of Biochem. and Pediat., Univ. of Saskatchewan, Saskatoon, Canada). *Canad. J. Biochem. Physiol.*, 1957, **35** (12), 1249-1258.—Prepared Dowex 1-X8 resin in equilibrium with 0.1 *M* acetate buffer (pH 4.0 to 4.6) in a column 10 mm \times 70 mm to 150 mm is used. Glutamic and aspartic acids are eluted and separated with the same buffer soln. (pH 4.0 to 4.6), into a fraction collector; cysteic acid is then eluted with 0.2 *M* acetate buffer, pH 5.5 to 5.9. Determination in the eluates is made by the ninhydrin method of Moore and Stein (*Anal. Abstr.*, 1955, **2**, 986). The results are reported of application of the method to hydrolysates of various proteins, normal protein-free plasma, and normal urine. H. F. W. KIRKPATRICK

3095. Paper-chromatographic method for estimation of phenylalanine. H. K. Berry (Dept. of Pediatrics, Coll. of Med., Univ. of Cincinnati, Ohio). *Proc. Soc. Exp. Biol. Med.*, 1957, **95**, 71-73.—Deproteinise 0.5-ml samples of blood serum with 4 vol. of 95% ethanol and carry out paper chromatography in comparison with aq. standards of D-phenylalanine containing 0.2, 0.3 and 0.4 μg per ml. Develop with a solvent mixture of *n*-butanol-ethanol (95%) - water (70:20:20) for ≈ 6 hr. Dry in air and spray with a reagent prepared by adding 200 μg of ninhydrin to 85 ml of *n*-butanol, 10 ml of water and 5 ml of 95% ethanol. Heat the sheets in an oven at 90° for 10 min. Phenylalanine appears as a blue spot at R_F 0.42. Other amino acids give purple spots and travel to different positions. The determination can be made by visual comparison or with a densitometer. The method can also be used for spinal fluid and urine. The recovery averages 95%. G. F. SOMERS

3096. Ultra-micro analysis of total nitrogen of peptides and amino acids isolated by paper chromatography or electrophoresis. P. Baudet and E. Cherbuliez (Lab. Chim. Org. et Pharm., Univ. Genève). *Helv. Chim. Acta*, 1957, **40** (6), 1612-1620 (in French).—After degradation at 450° in sealed capillary tubes with 50% (v/v) aq. H_2SO_4 containing 0.2% of $HgCl_2$, the amino-acid and polypeptide N (1 to 8 μg) in 10 μl of eluate from chromatograms or electropherograms can be assayed colorimetrically with ninhydrin. Results are in good agreement with those obtained by the micro-Kjeldahl method. M. DAVIS

3097. Detection of phenylthiohydantoins on paper chromatograms. K. R. Hanson and D. R. Whitaker (Nat. Res. Lab., Ottawa, Canada). *Chem. & Ind.*, 1958, **23**, 43.—Neither Feigl's sodium azide-iodine reagent nor Grote's reagent is entirely satisfactory for the paper-chromatographic detection of 5-substituted 3-phenyl-2-thiohydantoins (PTHs) prepared in the determination of N-terminal amino acids of proteins and peptides. A better method is to dip the dried and clean chromatogram for 30 sec. in a soln. of 0.1 *N* $KMnO_4$ and 0.2 *N* H_2SO_4 , and then wash the paper immediately in running water until the purple colour is removed. The PTHs are then revealed as brown spots of MnO_2 (these are coloured blue by a soln. of benzidine in dil. acetic acid). The sensitivity of the test is 0.01 $\mu mole$ on washed Whatman No. 1 paper and 0.02 $\mu mole$ on unwashed paper. A suitable amount of sample for chromatographic separation and detection is 0.05 $\mu mole$ (as PTH). W. J. BAKER

3098. Determination of serum albumin and globulin by a new method. J. R. Debro, H. Tarver and A. Korner (Calif. Univ. Med. Sch., Berkeley, U.S.A.). *J. Lab. Clin. Med.*, 1957, **50** (5), 728-732.—The method is based on the selective pptn. of serum globulin by 1% trichloroacetic acid in 96% ethanol, by which the albumin is not pptd. Total protein is determined colorimetrically with Folin-Ciocalteu reagent on one dilution of the sample, and the albumin is determined on an aliquot of the supernatant liquid after removal of globulin. The method is suitable for use on a micro scale and gives a rectilinear calibration with 25 to 125 μ g of protein. W. H. C. SHAW

3099. Oscillographic polarography of steroids. V. Morávek, Z. Kadaňka and L. Minářová (Biochem. Inst., Masaryk Univ., Brno, Czechoslovakia). *Publ. Fac. Sci. Univ. Masaryk*, 1957, (387), 401-428 (in English).—An isopropyl alcohol soln. (4 ml) of the chemically pure steroid is placed in the mercury anode vessel, 1 ml of 5 N HCl is added and polarography is carried out with a dropping mercury electrode and an oscilloscope. Characteristic oscillograms were observed with several steroids. Cholesterol can be determined accurately in 1 ml of a 0.005% soln. H. F. W. KIRKPATRICK

3100. Simultaneous determination of cortisol and corticosterone in human plasma by quantitative paper chromatography. P. K. Bondy and G. V. Upton (Dept. of Med., Yale Univ., New Haven, Conn.). *Proc. Soc. Exp. Biol. Med.*, 1957, **94**, 585-589.—The steroids are extracted with CHCl_3 , purified by two-stage paper chromatography and identified in u.v. light. The spots are cut out, eluted with ethanol and determined fluorimetrically. Corrections are made for losses incurred by the addition of the radioactive steroids [$4\text{-}^{14}\text{C}$]cortisol and [$4\text{-}^{14}\text{C}$]corticosterone. The normal amount of cortisol in human plasma is $10.2 \pm 3.6 \mu\text{g}$ per 100 ml and corticosterone $1.3 \pm 2.5 \mu\text{g}$ per ml. G. F. SOMERS

3101. Determination of β -glucuronidase activity in urine. M. A. M. Abul-Fadl (Chester Beatty Res. Inst., London). *J. Clin. Path.*, 1957, **10** (4), 387-389.—Modifications of the method of Talalay *et al.* (*J. Biol. Chem.*, 1946, **166**, 757) are described. H. F. W. KIRKPATRICK

3102. Simple methods of measuring serum levels of the glutamic-oxaloacetic and glutamic-pyruvic transaminases in routine laboratories. A. F. Mohun and I. J. Y. Cook (New End Hosp., London). *J. Clin. Path.*, 1957, **10** (4), 394-399.—Direct colorimetric methods without protein pptn. or toluene extraction are described. H. F. W. KIRKPATRICK

3103. Photometric determination of reducing substances [in nutrient media]. B. Matkovics and E. Kovács (Org. Chem. and Biochem. Inst., Univ., Szeged, Hungary). *Naturwissenschaften*, 1957, **44** (23), 616.—The method is recommended for the determination of reducing substances in nutrient media. The copper and alkali reagent are those of Schoorl (*Chem. Weekbl.*, 1929, **26**, 130) and comprise reagent (A) 69.28 g of CuSO_4 per litre, and reagent (B) 364 g of Na K tartrate and 100 g of NaOH in one litre of water. To a 50-ml flask is added 1 to 20 ml of medium containing 70 to 90 mg of sugar, followed by 10 ml of each reagent A and B. The flask is held in a boiling-water bath until the Cu_2O

has separated, then the contents are cooled and made up to the mark with water. After the ppt. has settled, the supernatant liquid is poured off and its extinction is measured in a Pulfrich photometer. Suitable calibration curves are constructed, with sugar-free media as blanks. E. KAWERAU

See also Abstracts—**3017.** Paper chromatography of methylated D-glucosamine, D-galactose and D-mannose. **3018.** Infra-red identification of disaccharides. **3023.** Paper chromatography of volatile fatty acids. **3126.** Quant. i.r. analysis of steroids. **3161.** Measurement of amylolytic activity. **3169.** Determination of vitamin A and tocopherol in calf livers. **3171.** Determination of flavins. **3192.** Determination of the fungicide Karathane in animal tissues.

Drugs

3104. Pharmaceutical analysis by polarography. XVI. Assay of morphine separated by ion-exchange method. Kazuo Matsumoto (Gifu Public Health Lab., Yatsuume-cho, Gifu). *J. Pharm. Soc. Japan*, 1957, **77** (4), 367-370.—Morphine (I) is adsorbed on Amberlite IRA-411 from an aq. methanolic soln. (Grant *et al.*, *J. Amer. Pharm. Soc.*, 1953, **42**, 150) and eluted with N HCl. The eluate is treated with HNO_3 and polarographed (*cf.* *J. Pharm. Soc. Japan*, 1952, **72**, 1393). Injection of papaveretum or opium tincture (10 ml) is mixed with 95% methanol (10 ml) and passed through a column of Amberlite IRA-411 (10 g) (2 ml per min.). The column is washed with 75% methanol (200 ml) and then water (200 ml) and eluted with N HCl. A 1-ml portion of the eluate (200 ml) is treated with N HCl (1.5 ml) and 1% KNO_3 soln. (1.5 ml) for 2 min. at room temp., then mixed with 20% KOH soln. (1.5 ml), bubbled with N for 1 min. and mixed with gelatin soln. (1.5%, 1 ml) before being polarographed. K. SAITO

3105. Quantitative determination of atropine-group alkaloids by titration in non-aqueous solvents. N. P. Dzyuba and M. S. Shraiber (Kharkov Chem.-Pharm. Res. Inst.). *Aptechnoe Delo*, 1957, **6** (6), 17-22.—The total alkaloids of the atropine group (atropine plus hyoscyamine plus hyoscine) are determined by titration against HClO_4 in anhydrous acetic acid. The method is applied to leaves, extract and tincture of belladonna, and to tablets, suppositories and eye-drops containing atropine or belladonna. The end-point is determined potentiometrically (quinhydrone electrode with S.C.E. as comparison electrode) or with crystal violet as indicator. E. HAYES

3106. Colorimetric estimation of atropine and related alkaloids in pharmaceutical preparations. I. Nir-Grosfeld and E. Weissenberg (Gov. Inst. for Standardisation and Control of Pharmaceuticals, Min. of Health, Jerusalem, Israel). *Drug Standards*, 1957, **25** (6), 180-185.—Two colorimetric methods are given for the determination of atropine, hyoscyamine and [by method (b) only] hyoscyamine in pharmaceutical preparations. Recovery experiments indicate an accuracy of $\pm 1\%$. The results agree with those obtained by the method of the U.S.P. XV. *Procedure (a)*—Prepare a CHCl_3 extract by the U.S.P. method. Evaporate an aliquot (containing 0.25 to 1 mg of alkaloid) to dryness on a water bath, add

fuming HNO_3 (0.3 ml), heat until fuming ceases, dry at 105° for 15 min. and allow to cool. Dissolve the residue in acetone and dilute to 25 ml. Mix a 5-ml aliquot with isopropylamine (2 ml) and 0.1% methanolic KOH (0.1 ml) and after 1 min. measure the extinction at 540 $\text{m}\mu$. **Procedure (b)**—Prepare the nitro compound as in (a) and dissolve it in 50% ethanol (10 ml). Heat on a water bath with 10% HCl (2.5 ml) and zinc dust (0.1 g) for 10 min., cool and filter, wash the zinc residue with H_2O (2×4 ml) and add the washings to the filtrate. Add 1% NaNO_3 (1 ml), mix and allow to stand for 10 min. Add 2.5% ammonium sulphamate soln. (1 ml), shake and allow to stand for 10 min. Add 1% N-1-naphthylethylenediamine dihydrochloride soln. (1 ml), dilute with H_2O to 25 ml, and after 30 min. measure the extinction at 550 $\text{m}\mu$. Calculate by reference to a standard curve. A. R. ROGERS

3107. Comparison of the results of the assay of an extract of belladonna by volumetric methods and the modified Vitali-Morin method. M. P. Febvre (Fac. de Méd. et de Pharm., Clermont-Ferrand, France). *Ann. Pharm. Franç.*, 1957, **15** (11), 638-639.—The results obtained with an extract of belladonna by the modified Vitali-Morin reaction (*cf. Anal. Abstr.*, 1958, **5**, 3108) are compared with those obtained by the volumetric methods of the Fr. Codex, the International Pharmacopoeia, and Hegnauer and Flück (*Pharm. Acta Helv.*, 1948, **23**, 246). The lowest result is given by the Vitali-Morin reaction as this is specific for atropine-type alkaloids. E. J. H. BIRCH

3108. The Vitali reaction as a quantitative reaction. M. P. Febvre (Fac. de Méd. et de Pharm., Clermont-Ferrand, France). *Ann. Pharm. Franç.*, 1957, **15** (11), 635-637.—The Vitali-Morin reaction for atropine, hyoscyamine and hyoscyne is modified to give a reproducible colour that can be used quantitatively. **Procedure**—A known vol. of the sample is evaporated to dryness under vacuum in a centrifuge tube, then treated with a few drops of a mixture of 7 ml of H_2SO_4 (66° Bé) and 2 ml of fuming HNO_3 and stirred to make the soln. homogeneous. Acetone (2 ml) is added and 10% abs. ethanolic KOH (the presence of water or methanol vitiates the reaction) drop by drop until the soln. is neutralised, when the colour appears at once. After centrifugation to remove solids pptd. by the acetone and making up to 10 ml with acetone, the extinction is measured (Filter 63 of the Jobin-Yvon spectrophotometer). The extinction is stable for 10 min. at 20° . The Beer-Lambert law is followed only for concn. from 5 to 20 μg per ml, but for higher concn. a calibration curve can be used. Above 100 μg per ml the sensitivity falls off. The mean error is $\approx 1\%$. No colour is given by the hydrolysis products of these alkaloids. E. J. H. BIRCH

3109. Colour reaction given by some derivatives of colchicine in the presence of nicotinic or isonicotinic [acid] hydrazide. M. Pesez (Serv. de Rech., Roussel-Uclaf, Paris-Romainville, France). *Ann. Pharm. Franç.*, 1957, **15** (11), 630.—Colchicine in dil. aq. soln. (5 ml) is treated with 2 ml of 10% aq. isonicotinic acid hydrazide and 1 ml of 10% Na_2CO_3 soln. A yellow-orange colour (absorption max. 450 $\text{m}\mu$) develops in 10 min. on a boiling-water bath, and obeys Beer's law for samples between 10 and 70 μg . The limit of sensitivity is 1 μg . The product of reaction with colchicine itself is colchicine isonicotinoylhydrazide, which has been isolated.

The reaction is also given by colchicoside, 2-demethylcolchicine, demecolcine (N-methyldeacetylcolchicine), and isocolchicine. Thiocolchicine and its derivatives give a very slight reaction and the reaction of colchicine is negative. Nicotinic acid hydrazide and Girard's reagent T give a similar reaction with colchicine. E. J. H. BIRCH

3110. Determination of alkaloids from *Rauwolfia serpentina* Benth. I. Separation of reserpine from total alkaloids by paper electrophoresis. Kazutaka Yamaguchi, Hatsue Shoji and Kazumitsu Nishimoto (National Hygienic Lab., Tamagawa-yoga, Setagaya-ku, Tokyo). *J. Pharm. Soc. Japan*, 1957, **77** (4), 337-340.—After the paper electrophoresis (700 V per 33 cm, 0.3 to 0.4 mA per cm, 2 hr., 25°) of alkaloids from *Rauwolfia serpentina*, nine spots were detected by fluorescence. Reserpine (I) exhibits 3 spots by the use of 5 N acetic acid as developer. I is extracted with CHCl_3 from an aq. soln. at pH 6.5 and gives a distinctive spot by similar electrophoresis. Its CHCl_3 soln. gives two absorption peaks at 268 and 295 $\text{m}\mu$. The fluorescence of the spot appears 1 hr. after developing, and a new absorption appears simultaneously at 380 $\text{m}\mu$.

II. Fluorimetric determination of reserpine on filter-paper. Kazutaka Yamaguchi, Yoshikazu Tabata and Hatsue Shoji. *Ibid.*, 1957, **77** (4), 341-346.—The fluorimetric determination of I (McMullen *et al.*, *J. Amer. Pharm. Soc., Sci. Ed.*, 1955, **44**, 446) was applied to the determination of I in the spot. Both the spectrum and the intensity of the fluorescence change according to the treatment of the spot. When the spot (diameter 10 mm) is heated in an air bath (105°) in the vapour of 5 N acetic acid and 3% H_2O_2 for 1 hr., the intensity of the fluorescence at $500 \pm 50 \text{ m}\mu$ linearly increases with the amount of I ($< 1.5 \mu\text{g}$). K. SAITO

3111. Application of ion-exchange resins in medical analysis. IV. Determination of berberine chloride by cation-exchange resins. Hyozo Watanabe and Masanobu Yamasaki (Yamagata Kogyo Koko, Midori-cho, Yamagata). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (11), 1591-1594.—Berberine chloride (I) ($> 50 \text{ mg}$) is quant. adsorbed on a column (diam. 1 cm; length, 43 cm) of Amberlite IRC-50 (50 to 100 mesh) and the Cl^- in the eluate are titrated with AgNO_3 with fluorescein (0.2% in ethanol) as indicator. Washing with 20 ml of water suffices for complete removal of Cl^- from the column. The weakly basic (pH 9.0 to 9.6) eluate is neutralised (phenol red) with 0.1 N HNO_3 before the titration. K. SAITO

3112. Colorimetric determination of sparteine in broom (*Sarothamnus scoparius* L. Wimm.) by means of Reinecke's salt. F. Kaczmarek (Dept. of Plant Drug Analysis and Technol., Poznań). *Biul. Inst. Roślin Leczniczych*, 1957, **3** (4), 275-284.—An extensive summary of existing methods of determining sparteine is given. The present rapid method is based on that of Jaretsky and Axer (*Arch. Pharm., Berlin*, 1934, **272**, 152), with which it is compared. Experimental results are given on the effect of temp. and vol. on the quant. pptn. of sparteine with Reinecke's salt, and an improved method of extraction from the raw material is described. Sparteine, finally obtained as sulphate in acid soln., is pptd. with a 4% soln. of Reinecke's salt at 5° and under fairly strict conditions. The ppt. is dissolved in aq. acetone and its extinction

(at 533 $m\mu$) is measured and referred to a standard curve. The colorimetric reading can be taken within 2 hr. of the prepn. of the soln. The method is suitable for 2 to 20-mg amounts of sparteine, but as little as 0.05 mg can be determined. Results agree closely with those of the original method, the highest divergence in a set of 8 results being 5%.

T. M. M.

3113. Nicotyrine and its determination by the König reaction. M. De Clercq and R. Truhaut (Lab. de Toxicol. et d'Hyg. Ind., Fac. de Pharm., Univ. de Paris, France). *Ann. Pharm. Franç.*, 1957, **15** (9-10), 529-533.—The König reaction for pyridine deriv., in which BrCN is added to the N atom and the ring split with an arylamine to a coloured condensation product of glutaric aldehyde with the amine, is applied to nicotyrine [N-methyl-2-(pyrid-3-yl)pyrrole], which is a constituent of tobacco smoke. The speed of formation and stability of the colour is measured for nicotyrine and for nicotine for concn. of the free base from 5 to 500 μg with aniline, benzidine, 1- and 2-naphthylamines, diphenylamine, or 5-aminoacenaphthene. Only aniline is suitable for the determination of nicotyrine in the highest sensitivity range.

E. J. H. BIRCH

3114. Chromatographic determination of steam-volatile acids in cigarette smoke. L. D. Quin, P. Wilder, jun., and M. E. Hobbs (Duke Univ., Durham, N.C., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 546-547.—The unidentified acid fraction following formic acid on partition chromatography of the steam-volatile acids of cigarette smoke (cf. Buyske *et al.*, *Anal. Abstr.*, 1957, **4**, 1958) was derived from materials used in the analysis and not from the smoke sample. About 70% of this fraction consisted of glycine and at least one other acid was present. The sodium salts of the volatile acids were chromatographed in the same manner as the ammonium salts, and well-defined spots were obtained after ninhydrin treatment. R_F values for these salts are listed.

G. P. COOK

3115. Determination of purine derivatives in non-aqueous medium. I. B. Salvesen (Univ. Farm. Inst., Oslo, Norway). *Medd. Norsk Farm. Selsk.*, 1957, **19** (12), 199-209.—*Procedure*—A sample of 0.4 g of caffeine and sodium salicylate is dissolved in 10 ml of hot acetic anhydride. The soln. is cooled and 20 ml of benzene and 4 drops of 0.1% Tropaeolin OO in acetic acid are added as indicator. Titration with 0.1 N $HClO_4$ in acetic acid to an orange end-point gives the titre for sodium salicylate. Eight drops of 0.1% methyl violet in acetic acid are added and further titration to a golden-yellow end-point gives the titre for caffeine. For caffeine and sodium benzoate, 2 to 5 ml of acetic acid is added to the acetic anhydride to dissolve the sample. With mixtures of caffeine and diphenhydramine hydrochloride, methyl red (red end-point) is used in place of Tropaeolin OO to indicate the titration of the diphenhydramine. When hydrochlorides are present, a solution of mercuric acetate in acetic acid is added to the solvent. Potentiometric titration curves are shown.

E. J. H. BIRCH

3116. Photo-nephelometric determination of caffeine. V. N. Bernshteln (Pyatigorsk Pharm. Inst.). *Zhur. Anal. Khim.*, 1957, **12** (6), 744-748.—The method is based on the use of tungstophosphoric acid. A calibration curve is obtained by mixing

2 ml of 0.01 M sodium tungstophosphate, 4 ml of 2.5 M HNO_3 and various amounts (0.5 to 2.5 ml) of 0.001 M caffeine, then diluting to 50 ml and examining in a photo-nephelometer. Other materials in tea leaves do not interfere with the determination of caffeine. A modification enables the method to be used in the presence of various drugs.

G. S. SMITH

3117. Determination of micro quantities of alkaloids by the amperometric method. VII. Titration of caffeine, cinchonine and amidopyrine in hydrochloric acid solution with tungstosilicic acid. Tadahiko Ogawa (Fac. of Engng, Yokohama Univ., Minami-ku). *J. Electrochem. Soc. Japan*, 1957, **25** (7), 377-380.—An amperometric titration of caffeine (I) (at -0.70 V vs. the S.C.E.), cinchonine (II) and amidopyrine (III) (both at -0.75 V), similar to that for codeine (cf. *Anal. Abstr.*, 1957, **4**, 2356), can be made in >0.5 N HCl soln. The reaction between tungstosilicic acid and the alkaloids proceeds swiftly, in a molar ratio 1 to 2 for I and III, and 1 to 3 for II. The error is $<2\%$ for <35 mg of the alkaloids.

K. SAITO

3118. Chemical assay of *Digitalis purpurea* leaves. D. H. E. Tattje (Lab. voor Pharmacognosie, Rijksunivers. Groningen, Holland). *Pharm. Weekbl.*, 1957, **92** (24), 877-885.—Various chemical methods for the assay of digitalis leaves are reviewed and the following is recommended. *Procedure*—Allow 0.5 g of powdered leaf to swell in water and then transfer it to a weighed flask and make up to 50.5 g with water. After 1 hr. of mechanical shaking, add 5 g of 15% w/w Pb acetate soln. and filter. To 33 g of the filtrate add 4.5 g of 5% $Na_2HPO_4 \cdot 2H_2O$ soln., and filter. To 20 g of this filtrate (≈ 0.16 g of leaf) add 2 ml of 4 N HCl and boil under reflux for 30 min. Transfer the cooled liquid to a separating funnel, adding the washings from the condenser and flask (2×5 ml of water); shake with $CHCl_3$ (3×22.5 ml). The combined extracts are dried over Na_2SO_4 and filtered, and the filter is washed with dry $CHCl_3$ (3×5 ml). Divide the resulting soln. into 2 equal parts in 2 small flasks and evaporate. Determine the gitoxygenin in one residue by dissolving it in 10 ml of a mixture of H_2SO_4 and H_3PO_4 (37.5:62.5, by wt.) containing 0.05% of $FeCl_3 \cdot 6H_2O$. Warm the mixture for 9 min. on a water bath at 65° and determine the colour of the cooled soln. in a 0.5-cm cell at 570 $m\mu$ with a slit width of 40 Å. The standard deviation varies from ± 0.0017 to ± 0.0056 on percentages of gitoxygenin from 0.16 to 0.185. Dissolve the residue in the second flask in 4 ml of ethanol, 96% by vol., freed from aldehyde according to U.S.P. XIII, and add 5 ml of ethanolic 0.075% (w/v) 2,4-dinitrodiphenylsulphone soln. Mix and add 1 ml of freshly prepared 0.15 N NaOH. Measure the colour ≈ 3 min. after the addition of the NaOH, at 600 $m\mu$ in a 0.5-cm cell, with a 40-Å slit. This second determination gives total aglycone content (digitoxigenin and gitoxygenin), hence the digitoxigenin content can be calculated. The standard deviation is ± 0.0022 to ± 0.0053 on contents of 0.14 to 0.16%. The extinction coefficients and molar extinctions for several colours given by various digitalis glycosides with different reagents are given in tabular form.

P. HAAS

3119. Gravimetric methods of determination of santonin in drugs. M. Rasim Tulus and Ayhan Ulubelen (Inst. Anal. Chem. and Toxicol., Univ. Istanbul, Turkey). *Arch. Pharm., Berlin*, 1957,

290 (11), 527-532.—The paper-chromatographic and colorimetric method described previously (cf. *Anal. Abstr.*, 1956, **3**, 3745), adsorption chromatography on alumina-activated carbon, and polarimetry have been used in a critical study of 5 methods for the gravimetric determination of santonin. The purity of the final ppt. and the amounts of santonin remaining in the marc, on the chromatographic column and in the mother liquors have been determined in each case. The results obtained by the method of Janot and Mouton (*Bull. Sci. Pharmacol.*, 1936, **43**, 708) are 22% high; those obtained by the method of Kassner *et al.* (cf. *Brit. Abstr. C*, 1953, 398) are 2.5% low. The methods of Qazilbash (cf. *Brit. Abstr. C*, 1951, 264, and *Anal. Abstr.*, 1956, **3**, 1484) and that of Eder and Schreiner (*Schweiz. ApothZtg*, 1925, **63**, 453), which is used by D.A.B. VI, give the correct results after application of the specified correction factors.

A. R. ROGERS

3120. Test organisms for antibiotic microbiological assays. F. W. Bowman (Food and Drug Admin., Washington, D.C., U.S.A.). *Antibiot. & Chemother.*, 1957, **7** (12), 639-640.—The 19 organisms generally used, their common assay applications and their numbers in the ATCC, FDA and former PCI (Penicillin Control and Immunology) are reviewed.

W. H. C. SHAW

3121. Determination of chloramphenicol. I. A colorimetric determination with hydroxylamine hydrochloride and ferric chloride. Tsutou Aihara, Hideko Machida and Yuki Yoneda (Shinagawa Plant, Sankyo Co., Nishi-shinagawa, Shinagawa-ku, Tokyo). *J. Pharm. Soc. Japan*, 1957, **77** (12), 1318-1321.—The hydroxamic acid method (Soloway and Lipschitz, *Anal. Chem.*, 1952, **24**, 898; Bergmann, *Ibid.*, 1952, **24**, 1367) for the determination of chloramphenicol (I) was applied to the assay of aged samples. Decomposition products of I do not interfere with this method, although they vitiate the u.v. spectrophotometric method. The sample soln. (≈ 3 ml) containing < 8 mg of I is warmed (60°) with hydroxylamine hydrochloride (2 N, 0.5 ml) and NaOH (2.5 N, 0.5 ml) for 10 min., then cooled to 10° and treated with HCl (2.5 N, 0.5 ml) and FeCl_3 (1% in 0.1 N HCl) (2 ml). The extinction is measured at $505 \text{ m}\mu$ within 5 min.

II. Determination of chloramphenicol by paper electrophoresis. Tsutou Aihara and Kazuo Sato. *Ibid.*, 1957, **77** (12), 1322-1323.—I is separated from its decomposition products, which interfere with the u.v. spectrophotometric method, by electrophoresis in an acetate buffer (pH 4.5, 0.05 M) (1 mA per cm for 2 hr.). The spots are detected by u.v. light or with SnCl_4 and *p*-dimethylaminobenzaldehyde in a mixture of ethanol, HCl and butanol. The corresponding areas from another paper ($10 \text{ cm} \times 40 \text{ cm}$) are cut out, and extracted with water (30 ml, 100° , 15 min.), and the extinction is measured at $278 \text{ m}\mu$.

K. SAITO

3122. Microchemical method for the determination of Sakaguchi-positive antibiotics. I. Szilágyi and I. Szabó (Dept. of Antibiotics, Res. Inst. of Expt. Med. Sci., Hungarian Acad. Sci., Debrecen). *Nature*, 1958, **181**, 52-53.—The colour test for arginine with 1-naphthol and hypobromite (Sakaguchi, *Biochem. J.*, 1925, **5**, 25) has been applied to the determination of streptomycin, primycin and viomycin, with N-bromosuccinimide as a source of nascent hypobromite. For analysis, all solutions are cooled to 0° for 30 min., then 5 ml of test soln. is treated with

2 ml of naphthol reagent (5 ml of 0.2% ethanolic 1-naphthol made up to 100 ml with 10% aq. NaOH; stable for 7 days at 0°). After being shaken and set aside for 3 min., the mixture is rapidly poured into 0.5 ml of N-bromosuccinimide soln. (0.448% in 10% ethanol; stable for 5 days at 0°), the mixture is shaken vigorously and 1 ml of 40% urea soln. is added in 15 sec. A vivid red colour develops, the extinction of which is read in 5 min. against blanks, with a blue filter, results being referred to standard curves. The relative error of the method is $\pm 4\%$. Arginine and Sakaguchi-positive antibiotics can be detected in paper chromatograms by dipping the paper in 0.01% 1-naphthol in 5% methanolic NaOH, drying in air, spraying with cooled 0.5% N-bromosuccinimide and stabilising with 40% urea.

R. E. ESSERY

3123. Characterisation and determination of streptidine in streptomycin and dihydrostreptomycin. J. Philippe, Y. Jolchine and O. Alcaraz (Lab. de la S.I.F.A. et de la Soc. des Antibiotiques de France, La Plaine Saint-Denis, Paris). *Ann. Pharm. Franç.*, 1957, **15** (9-10), 546-553.—Samples of streptomycin and dihydrostreptomycin are subjected to electrophoresis on paper (Whatman 3MM, $1 \text{ cm} \times 37 \text{ cm}$) in a borate buffer (borax 7.6 g, H_3BO_3 1.25 g, NaCl 0.3 g, water to 1 litre) at pH 9. The electropherogram is run for 3 hr. at 500 V and the spots are developed with Monastero's alkaline nitroprusside-ferricyanide reagent (*Brit. Abstr. C*, 1952, 448). The streptidine spot is well separated and clearly visible if it contains $< 2 \mu\text{g}$. A calibration curve can be established in which log length of spot against log weight of streptidine is linear. The streptidine content is determined in several streptomycin and dihydrostreptomycin samples.

E. J. H. BIRCH

3124. Rapid determination of the relative purity of vitamin B₁₂ (cyanocobalamin) in pharmaceutical products. C. F. Bruening, W. L. Hall and O. L. Kline (Food and Drug Admin., Dept. Health, Educ. and Welfare, Washington, D.C., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (1), 15-20.—Pure cyanocobalamin (I) shows values of $E_{1\text{cm}}^{1\%}$ at $341 \text{ m}\mu$ and $376 \text{ m}\mu$ of 80.4 and 80.9, respectively; the average ratio $E(341 \text{ m}\mu)/E(376 \text{ m}\mu) = 0.990$. The following max. values are suggested to limit the amount of "red pigments" in injections made from I— $E(341 \text{ m}\mu)/E(376 \text{ m}\mu) > 1.020$, $E_{1\text{cm}}^{1\%}(341 \text{ m}\mu) > 83.0$, $E_{1\text{cm}}^{1\%}(376 \text{ m}\mu) > 82.5$. The validity of the procedure was established by comparing results with the purity index found by a combination of tracer and spectrophotometric ($361 \text{ m}\mu$) methods. The average difference between duplicate determinations of the extinction ratio was 0.6%.

A. R. ROGERS

3125. Polarographic studies of pharmaceuticals. IX. Polarography of camphor derivatives. (v). The relationship between the reduction potential and chemical structure, and analytical applications. Yutaka Asahi (Res. Lab., Takeda Pharm. Ind., Jusonishinocho, Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1957, **77** (2), 145-148.—The fact that only 3-, 6-, 8-oxocamphor (1:7-dimethyl-2-oxonorcamphane-7-aldehyde) and 10-oxocamphor (2-oxoapocamphane-1-aldehyde) and 3-halocamphor provide reduction waves and that their diffusion-current constant (K_D) falls between 1.94 and 2.94 indicates the participation of two electrons in the reduction. The temp. coeff.

($\approx 1.7\%$ per 1°) shows that the limiting current barely affects kinetic current. The wave heights are proportional to concn. of the camphor derivatives. No interference results from reduction products such as isoketopinic acid (1:7-dimethyl-2-oxonorcamphane-7-carboxylic acid). 3-Oxo-, 3-bromo- and 3:8-dichloro-camphor are determined simultaneously because their $E_{1/2}$ values differ. Although 8-, 10- and 6-oxocamphor have similar $E_{1/2}$ values, they are determined polarographically by making use of their different stabilities (8->10->6-oxocamphor) in alkaline soln. Their sum ($\approx 0.001 M$) is determined at pH 6.8 by the measurement of the overall wave height at -1.6 to $-1.8 V$. When the sample soln. containing these three is bubbled with N in a borate buffer of pH 9.7 at 25° for 30 min., 6-oxocamphor is decomposed and the wave height of the resulting soln. corresponds to the sum of 8- and 10-oxocamphor. When the sample soln. is bubbled similarly in 0.1 N NaOH, only 8-oxocamphor remains unchanged and is similarly determined polarographically, after neutralisation with HCl.

K. SAITO

3126. Quantitative analysis of steroid preparations by infra-red spectroscopy. Akira Ito and Osamu Amakasu (Takamine Res. Lab., Sankyo Co., Nishishinagawa, Shinagawa-ku, Tokyo). *J. Pharm. Soc. Japan*, 1957, **77** (10), 1083-1086.—Oestradiol (I) in CS_2 and ethisterone (II) in $CHCl_3$ are determined by the use of key bands at 1748 cm^{-1} and 1064 cm^{-1} , and 1667 cm^{-1} and 3333 cm^{-1} , respectively. The working curve is linear for $<2\text{ mg}$ per ml. Since these bands are due to the functional groups at the 3- and 17-positions for I, and 3- and 20- for II, progesterone and methyltestosterone can be similarly determined by the use of key bands at 1709 and 1678 , and 1678 and 1085 cm^{-1} , respectively. Ethinyloestradiol, which is insol. in CS_2 and $CHCl_3$, is made into a potassium bromide tablet and determined with key bands at 1504 and 818 cm^{-1} . The coeff. of variation is 1.0 to 1.8% in soln. and $\approx 2\%$ in the potassium bromide tablet.

K. SAITO

3127. Polarimetric determination of 17-hydroxyprogesterone caproate in benzyl benzoate - castor oil. V. Gerosa and M. Melandri (Soc. Ital. Prod. Schering, Milan). *Ann. Chim., Roma*, 1957, **47** (12), 1388-1393.—17-Hydroxyprogesterone caproate (I) dissolved in a mixture of benzyl benzoate (II) and castor oil (III) may be estimated polarimetrically without recourse to three-dimensional graphs. Curves are plotted of the rotation against concn. of I in II, in III, and in II plus III, and from these is prepared in the indicated manner a two-dimensional projection from which the concn. of I may be determined.

A. G. COOPER

3128. Estimation of organic sulphur in asafetida. L. V. L. Sastry (Central Food Tech. Res. Inst., Mysore, India). *J. Sci. Ind. Res., B, India*, 1957, **16** (11), 508-510.—*Procedure*—The powdered sample (0.5 g) is mixed with H_2O (250 ml), and a 1-ml aliquot of the resulting suspension is placed in a 50-ml flask. *p*-Aminodimethylaniline hydrochloride (0.2% soln. in $2 N H_2SO_4$) (3 ml), $2 N H_2SO_4$ (40 ml) and zinc dust (50 mg) are added, the flask is stoppered and the contents are mixed and set aside for 12 hr. at room temp. To the flask is added $FeNH_4(SO_4)_2 \cdot 12H_2O$ soln. (56.5 g in 250 ml of $N H_2SO_4$) (3 ml) and the mixture is shaken and

set aside for 30 min. The vol. is made up to 50 ml with $2 N H_2SO_4$, the soln. is centrifuged, and the extinction of the blue supernatant soln. is measured at $670 m\mu$. The readings are corrected for a blank prepared in the same way.

C. A. SLATER

3129. Determination of chlorbutanol [chlorbutol] in pharmaceuticals by amperometric titration. J. L. Lach, D. Nair and S. M. Blaug (Coll. Pharm., State Univ., Iowa City, U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (1), 46-48.—Mix an aliquot of the sample soln. (2 ml containing 6 mg of chlorbutol) with acetone (20 ml), saturated NH_4NO_3 soln. (1 ml), 1% gelatin soln. (2 drops) and conc. HNO_3 (1 drop), and titrate amperometrically (rotating platinum electrode) with 0.08 N alcoholic $AgNO_3$. Mix another 2-ml aliquot with 5% NaOH soln. (2 ml) and allow to stand for 15 min., acidify with conc. HNO_3 and analyse as described above. The difference in the Cl^- content of the two soln. corresponds to the amount of Cl^- due to the chlorbutol present in the sample.

A. R. ROGERS

3130. Infra-red study of the reaction of barbiturates with *p*-nitrobenzyl chloride. L. G. Chatten and L. Levi (Food and Drug Lab., Dept. of Nat. Health and Welfare, Ottawa, Canada). *Appl. Spectroscopy*, 1957, **11** (4), 177-188.—In alkaline media, barbiturates react with *p*-nitrobenzyl chloride to give characteristic derivatives. The i.r. spectra indicate that the process of complex formation proceeds via the interaction of a negative enolised barbituric acid ion with a positive *p*-nitrobenzyl ion. The compounds show unique features throughout the region 2.5 to $16\text{ }\mu$, and this affords a positive means of identification of the various barbiturate drugs.

P. T. BEALE

3131. The chromatographic separation and determination of diphenylhydantoin and phenobarbitone. J. L. Lach, K. Bhansali and S. M. Blaug (Coll. Pharm., State Univ., Iowa City, U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (1), 48-49.—Prepare a chromatographic column (45 cm \times 2 cm) containing borate buffer (pH 9.2) as stationary phase on Celite 535. Mix the sample of diphenylhydantoin (I) (50 to 90 mg) and phenobarbitone (II) (8 to 40 mg) with H_2O (3 ml) and Celite 535 (3 g), and add $CHCl_3$ (5 ml) to form a slurry. Transfer the slurry to the column with the aid of two 5-ml portions of $CHCl_3$. Elute I with $CHCl_3$ (100 ml) and II with *n*-butanol- $CHCl_3$ (1:9) (100 ml). Determine the concn. of I and II in the eluates spectrophotometrically at $260 m\mu$. The mean recovery of I and II from capsules was 96.5% and 106.7%, respectively.

A. R. ROGERS

3132. The analysis of mixed preparations. I. Assay of phenacetin by the formation of indophenol. Takanobu Itai and Shozo Kamiya (National Hyg. Lab., Tamagawa-yoga, Setagaya-ku, Tokyo). *J. Pharm. Soc. Japan*, 1957, **77** (5), 554-556.—Phenacetin (I) ($\approx 100\text{ mg}$) is converted into *p*-aminophenol (II) by heating with HBr (46%, 5 ml) for 30 min.; II (corresponding to $<10\text{ }\mu\text{g}$ of I) is treated with *o*-cresol (1%, 1 ml) and 0.1 N NaOH (2 ml) and the resulting indophenol is measured at $605 m\mu$. The working curve is linear for $<10\text{ }\mu\text{g}$ of I. No interference results from acetanilide, acetylsalicylic acid, caffeine, amidopyrine or diphenhydramine hydrochloride. In the presence of phenyl salicylate, 1% phenol can be used as an alternative colour reagent (max. absorption $620 m\mu$).

K. SAITO

3133. Analysis of drugs and chemicals by infra-red absorption spectroscopy. II. Assay of amidopyrine in pharmaceutical products containing amidopyrine, phenacetin and caffeine. Naofumi Oi, Kazuko Kageyama and Kei-ichiro Miyazaki (Res. Dept., Osaka Works, Sumitomo Chem. Co., Kasugade-cho, Konohana-ku). *J. Pharm. Soc. Japan*, 1957, **77** (4), 439-440.—Amidopyrine (**I**) (<20 µg) is extracted with CS₂ (10 ml) from tablets or powder containing phenacetin (**II**) and caffeine (**III**); **II** and **III** remain practically undissolved with any starch present. The extinction of the CS₂ soln. at 14.46 µ is proportional to the concn. of **I** when measured against saturated CS₂ soln. of **II** and **III**. The error is $\pm 2\%$.

K. SAITO

3134. A simple method of detecting hydrolysis products in solutions of local anaesthetics of the procaine series. U. Zimmer (Pharmacy, Tuberculosis Sanatorium, Stralsund, Germany). *Dtsch. ApothZtg*, 1957, **97** (51-52); *Krankenhaus-Apotheker*, **7** (4), 26-29.—A sample containing ≈ 100 µg of procaine (**I**) (or analogue) is spotted on a filter-paper and dried at 50° to 60°. A wick of cotton wool is attached to the spot, and the lower end dips into *n*-butanol satd. with aq. NH₃. The developed paper chromatogram is dried and then sprayed successively with NaNO₂ dil. HCl and aq. ethanolic KOH - 2-naphthol, resulting in hydrolysis of **I** to a substituted *p*-aminobenzoic acid (**II**), diazotisation and coupling. Barbiturates, atropine, inorg. salts, caffeine, vasoconstrictors and K₂S₂O₈ do not interfere. The limit of detection is about 0.5 µg of **II**.

A. G. COOPER

3135. Cupric acetate reagent for sulphonamides. A. Goudswaard (Rijksinst. Pharmaco-therap. Onderzoek, Leiden, Netherlands). *Pharm. Weekbl.*, 1957, **92** (25), 913-914.—Four reagents suitable for differentiating commonly used sulphonamides are (i) a satd. soln. of cupric acetate (**I**) in ethanol; (ii) a mixture (100:2, by vol.) of (i) and 10% aq. NH₃; (iii) 0.1% aq. **I**, supplemented by warming and the addition of 0.1 N NaOH; (iv) a mixture (100:2, by vol.) of 0.1% aq. **I** and 10% aq. NH₃. The colour reactions are listed.

P. RENTENAAR

3136. Estimation of sulphonamides. K. N. Gaiind and D. P. Punn (Punjab Univ., Dept. Pharm., Med. Coll., Amritsar). *Indian J. Pharm.*, 1957, **19** (12), 279-281.—An acetylation method is described for the determination of sulphonamides in powders, tablets and injections. A sample is heated under reflux with a known amount of acetic anhydride in the presence of pyridine, then cooled, and an excess of N NaOH is added. The ppt. is filtered off and washed, and the excess of N NaOH in the filtrate is measured by titration of an aliquot with 0.04 N H₂SO₄ with phenolphthalein as indicator. A control is simultaneously carried out. The sulphonamide content is calculated from the acetic anhydride used up. A factor which is different for each sulphonamide is used. Modifications are described for special cases.

D. P. FELIX

3137. Iodimetric method for the determination of "Étazol" [2-(*p*-aminobenzenesulphonamido)-5-ethyl-1:3:4-thiadiazole]. A. Yu. Ibadov and G. A. Beseda (Tashkent Pharm. Inst.). *Aptechnoe Delo*, 1957, **6** (6), 57-59.—In acid soln. Étazol reacts with a soln. of iodine and KI to form a periodide,

C₁₀H₁₂O₄N₄S₂·3I.HI; the reaction is used for the quant. determination of Étazol. *Procedure*—Dissolve a weighed sample (to make a 0.1 N soln.) in 25 ml of 2 N HCl and make the soln. up to 100 ml. To a 20-ml aliquot of this soln. add 60 ml of 0.1 N iodine (containing 25 g of KI per litre); shake, and filter. Reject the first runnings of the filtrate and titrate the excess of iodine in a 25-ml aliquot of the remainder against 0.1 N Na₂S₂O₃.

E. HAYES

3138. Volumetric determination of the 4-aminosalicylate of isoniazid. J. A. Huerta Ortega and J. Candela Candela. *Monit. Farm. Terap.*, 1957, **63**, 429-430.—The method is based on hydrolysis of the sample with water and extraction of the 4-aminosalicylic acid (**I**) with ether. The isoniazid is determined iodimetrically and the **I** by means of the argentimetric technique given in the Spanish Pharmacopoeia IX.

T. R. MANLEY

3139. Quantitative determination of "Ftivazid" [N-4-hydroxy-3-methoxybenzylidene-N-isonicotinoylhydrazine]. M. E. Shub and N. S. Volkova (All-Union Scientific Chemico-Pharm. Res. Inst.). *Aptechnoe Delo*, 1957, **6** (6), 59-60.—Ftivazid is hydrolysed and the isoniazid formed is determined by oxidation with KIO₃. *Procedure*—A weighed sample (0.2 g) is heated under reflux for 30 min. with 50 ml of 20% H₂SO₄ and 25 ml of water in a 250-ml conical flask. The contents of the flask are cooled and transferred to a 250-ml separator; 50 ml of 0.1 N KIO₃ is added, the separator is shaken and 20 ml of CHCl₃ is added. After 3 min. the contents of the separator are shaken for 30 sec. and the CHCl₃ layer is separated. The aq. layer is further extracted with CHCl₃ (1 × 20 ml, 2 × 10 ml, and 2 × 5 ml); the final extract should be colourless. To the aq. layer 3 g of KI is added and the liberated iodine is titrated against 0.1 N Na₂S₂O₃. A blank experiment is carried out at the same time.

E. HAYES

3140. Estimation of piperazine in pharmaceutical preparations. R. V. Kamath, K. Gopal and S. B. Rao (Navaratna Pharm. Lab., Cochin 2). *Indian J. Pharm.*, 1957, **19** (12), 289.—Piperazine is determined by quant. pptn. with a satd. aq. soln. of ammonium reineckate at pH 9 to 10, dissolving the ppt. in pure acetone and measuring the extinction of the red soln. in a photo-electric colorimeter with a green filter.

D. P. FELIX

3141. Studies on the purity of dimercaprol (BAL). R. I. Ellin, A. A. Kondritzer and D. H. Rosenblatt (Army Chemical Center, Md., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (1), 12-14.—Variations in the toxicity of dimercaprol (**I**) are due to the presence of propane-1:2:3-trithiol (**II**) as impurity. Samples containing **II** are distinguished as follows—higher titre with iodine; higher refractive index; development of a yellow turbidity on mixing a soln. in dimethylformamide with a soln. of Pb acetate in pyridine; paper chromatography with the upper phase of a benzene-heptane-methanol-H₂O (1:1:1:1) mixture as solvent shows a band due to **II** at R_F = 0.93 as well as that due to **I** at R_F = 0.65.

A. R. ROGERS

3142. Detection of narcotics of the dialkylamino-dithienylbutene series. Shichiro Akiya, Yasuo Nakazawa and Shunji Ishikura (Tokyo Medico-Dental College, Yushima, Bunkyo-ku). *J. Pharm.*

Soc. Japan, 1957, **77** (8), 931-933.—Dimethylthiambutene hydrochloride and its methylethylamino and diethylamino homologues are decomposed with 30% H_2O_2 on a water bath; the product, di-2-thienyl ketone, is extracted with ether, washed with dil. HCl, dil. NaOH and water, converted into a 2:4-dinitrophenylhydrazone (max. absorption 403 m μ) and submitted to paper chromatography on a paper treated with silica (Keller, *J. Amer. Chem. Soc.*, 1950, **72**, 1867), with CCl_4 saturated with water as developer. To distinguish the three homologues, the aq. layer is treated with alkali in a Conway unit and the amines are identified by paper chromatography, with a mixture of butanol, acetic acid and water (4 + 1 + 5, by vol.). K. SAITO

3143. Potentiometric titration of diphenolic oestrogens belonging to the stilbene series. K. Backe-Hansen and A. Wickström (Norwegian Govt. Pharmacopoeia Lab., Oslo, Norway). *Medd. Norsk Farm. Selsk.*, 1957, **19** (12), 193-198 (in English).—Dienoestrol (I), stilboestrol and hexoestrol (II) are titrated with K methoxide or tetra-*n*-butylammonium hydroxide in pyridine or benzene-methanol solution. Potentiometric titration with the butylammonium hydroxide gives an inflection at 1 equiv. per mole and with K methoxide at 2 equiv. per mole only. Visual indication of the end-point, with azo violet as indicator, was possible in the butylammonium titrations with I and II, but the colour change is not sharp. Visual titration with K methoxide was possible only with I.

E. J. H. BIRCH

3144. Quantitative determination of "Pentoksil" (2:6-dihydroxy-5-hydroxymethyl-4-methylpyrimidine) and "Metatsil" (2:6-dihydroxy-4-methylpyrimidine). E. P. Balis (Naval Medical Academy). *Apteknoe Delo*, 1957, **6** (6), 55-57.—Pentoksil is determined by means of its reaction with hydroxylamine hydrochloride. *Procedure*.—To 50 ml of a soln. of Pentoksil (2.5 g in 500 ml) add 4 ml of a 10% soln. of hydroxylamine hydrochloride and titrate with 0.1 N NaOH, with a 0.1% ethanolic soln. of dimethylaminoozobenzene as indicator. Heat on a water bath for 30 min. and titrate the cooled soln. with 0.1 N NaOH. Carry out a blank titration at the same time. When Pentoksil is heated to 112° for 1.5 to 2 hr. it is quant. converted into 2:6-dihydroxy-4-methylpyrimidine and it can be determined gravimetrically in this way. Metatsil is determined iodimetrically. *Procedure*.—Dissolve a weighed sample (1.2 g) in 100 ml of water and 6 ml of 10% NaOH soln.; make the soln. up to 250 ml. To a 25-ml aliquot of this soln. add 25 ml of 0.1 N iodine and 5 ml of a 1% soln. of NaOH; set aside in the dark for 10 min. Add 5 ml of a 10% soln. of H_2SO_4 and titrate the liberated iodine against $Na_2S_2O_3$.

E. HAYES

3145. Quantitative determination of acetarsol by the method of back-titration. A. M. Aliiev (Azerbaidzhan Med. Inst.). *Apteknoe Delo*, 1957, **6** (6), 54-55.—Acetarsol is dissolved in 0.1 N NaOH and the excess of alkali is determined by back-titration with 0.1 N HCl, with phenolphthalein as indicator. For the determination of acetarsol in tablets, a sample is ground with 0.1 N NaOH at a temp. < 60°, and the excess of alkali is determined in the cooled soln.

E. HAYES

3146. A proposed test for purity of cyanocobalamin injection, U.S.P. H. L. Newark and M. Leff (Vitarine Co. Inc., 636 Eleventh St., New York,

U.S.A.). *Drug Standards*, 1957, **25** (6), 177-179.—A test is proposed to determine whether the cyanocobalamin (I) used to prepare injections of I complies with the requirement of 95% purity (anhydrous basis). Solutions of cobalamin concentrate N.F. show values of 50% to 75% purity by this method. *Procedure*.—Extract the sample (containing 5 to 10 mg of I) with a mixture of cresol- CCl_4 (1:1) (3×5 -ml portions). Wash the combined extracts with 0.1% aq. EDTA (disodium salt) soln. (10 ml) and H_2O (2×10 ml). Add acetone (100 ml) with constant stirring, then light petroleum (100 ml) and allow to stand for 1 hr. Filter through sintered glass, wash the ppt. with acetone, dry at 105° to 110° in a vacuum of 5 mm (Hg) for 2 hr. and weigh. Dissolve the ppt. in H_2O , dilute to 200 ml, and determine the I spectrophotometrically at 361 m μ .

A. R. ROGERS

3147. Determination of capsaicin in ointments and similar preparations. K. E. Schulte and H. M. Krüger (Pharm. Inst., Freie Univ., Berlin). *Arch. Pharm., Berlin*, 1957, **290**; *Mitt. dtsh. pharm. Ges.*, 1957, **27** (12), 202-205.—The earlier method for the quant. determination of capsaicin in drugs (cf. *Anal. Abstr.*, 1956, **3**, 515) is modified for application to ointments. The modifications consist of removal of substances which either interfere with the colour reaction or decrease the selectivity of chromatographic separation. If the ointment contains triglycerides, waxes or paraffins, 70% ethanol is used as solvent and beeswax is added to increase its selectivity towards capsaicin. If the ointment contains additional drugs such as salicylic acid, camphor or essential oils, the ether extract is treated with 1% NaOH soln. and the alkaline soln. is acidified with tartaric acid. The volatile constituents are then removed by steam-distillation and capsaicin is isolated from the aq. residue by successive treatments with ether, Na_2CO_3 soln. and ethanol.

M. H. SAWISTOWSKA

See also Abstracts—**3081.** Determination of digitoxin in tissues and excreta. **3082.** Determination of tetracycline and deriv. in body fluids. **3083.** Detection and determination of barbiturates in biological materials. **3084.** Determination of carbutamide and sulphonamides in blood-sugar filtrates. **3085.** Determination of carbutamide in blood. **3163.** Determination of dulcin. **3164.** Determination of capsaicin in paprika. **3165.** Determination of capsaicin.

Food

3148. Accurate determination of sugar colour. Anon. *Sugar, N.Y.*, 1957, **52** (6), 38, 40.—*Cf.* Deitz, *Anal. Abstr.*, 1957, **4**, 4115. S.C.I. ABSTR.

3149. Determination of reducing sugars by means of copper trihydroxyglutarate. A. V. Ablov and D. G. Bat'yr (Kishinev State Univ.). *Zhur. Anal. Khim.*, 1957, **12** (6), 749-753.—The method of Bertrand is used with trihydroxyglutaric acid replacing tartaric acid. Equal vol. of the soln. (A) 40 g of $CuSO_4 \cdot 5H_2O$ in 1 litre, and (B) 128 g of trihydroxyglutaric acid and 207 g of NaOH in 1 litre are used. Strict proportionality between the amounts of Cu_2O and reducing sugar is found.

G. S. SMITH

3150. The determination of copper in pectin. Z. Malkus, I. Schoberová and F. Fürst (Inst. Hyg., Prague). *Průmysl Potravin*, 1957, **8** (11), 594-596.
—Copper is determined polarographically in a soln. of aq. NH_3 and NH_4Cl . *Procedure*—Ignite the sample (1.5 to 3 g), cool and dissolve the ash in 6 N HCl (1 ml) and conc. HNO_3 (1 drop). Transfer the soln. by means of N aq. NH_3 into a 15-ml cylinder. Mix and separate the undissolved residue by centrifuging. To 10 ml of the supernatant liquid add a freshly prepared satd. soln. of Na_2SO_4 (0.2 ml) and gelatin soln. (0.5%) (3 drops) and register the polarographic wave from 0 to -0.6 V (mercury layer as anode). The results from the determination of 40 samples of pectin of various origins were in good agreement with those obtained photometrically with Na diethyldithiocarbamate.
J. ŽYKA

3151. The proximate analysis of wheat-flour carbohydrates. III. The estimation of the hemicellulose fraction. J. R. Fraser and D. C. Holmes (Dept. Gov. Chem., Clement's Inn Passage, London). *J. Sci. Food Agric.*, 1957, **8** (12), 715-721.—The presence of uronic acid groups in the hemicelluloses present in wheat bran interferes with their determination because of the formation of additional furfuraldehyde. The nature of the furfuraldehyde-yielding material in terms of arabinose, xylose and uronic acid is investigated. Factors are given for the conversion of the "xylose equivalent" into hemicellulose content. By using a previously advocated method (cf. *Anal. Abstr.*, 1957, **4**, 3442), the hemicellulose content of flour is given by its "xylose equivalent" multiplied by 0.97. H. B. HEATH

3152. Chemical determination of connective tissue in meat and its preparations. K. Möhler and N. Antonacopoulos (Dtsch. Forschungsanstalt für Lebensmittelchemie, München, Germany). *Z. Lebensmitteluntersuch.*, 1957, **106** (6), 425-440.—In examination of the amino acids in muscle flesh, organs, collagen and elastin, arginine, glycine and hydroxyproline were in greater proportion in collagen material. The content of hydroxyproline in meat and meat products may be determined and, by the application of suitable factors, may be used to calculate the total content of connective tissue protein. The sample is hydrolysed with HCl in the presence of SnCl_2 (cf. Wierbicki and Deatherage, *J. Agric. Food Chem.*, 1954, **2**, 878) for ≈ 7 hr., and the hydrolysate is oxidised by H_2O_2 in the presence of Cu^{2+} in alkaline medium. After acidifying and the addition of *p*-dimethylamino-benzaldehyde, a red colour is formed that has an absorption max. at 560 m μ . A test procedure with model sausages with additions of skin, tendon or collagen proved the value of the method.
S.C.I. ABSTR.

3153. Determination of the quality of lard on the basis of spectroscopy. H. P. Kaufmann, J. G. Thieme and F. Volbert (Inst. für Fettforschung, Münster, Westf., Germany). *Fette, Seif., Anstrichmitt.*, 1957, **59** (12), 1037-1048.—The spectroscopic method developed by Kaufmann *et al.* (*Anal. Abstr.*, 1957, **4**, 3122, 3123, 3452) for the detection of lard that has been refined with bleaching-earth is further studied. Samples of lard are subjected to heating, oxidation and bleaching, and the absorption curve of the original is subtracted from that of the treated lard over the range 220 to 300 m μ ; a plot of the log of this difference against wavelength gives a "difference curve," the shape of which indicates the

nature of the products resulting from the treatment. All the treatments studied produce a significant increase in absorption in the triene region, and the chromophores responsible for this increase cannot be removed by the usual refining methods; in particular, the value of $E_{268}^{1\%}$ at 268 m μ always increases. It is suggested that an upper limit for this value between 0.3 and 0.4 should be laid down for genuine lard.
E. HAYES

3154. Colorimetric determination of citrate in milk by [the method of] Babad and Shtrikman. G. K. Murthy and R. McL. Whitney (Illinois Univ., Urbana, U.S.A.). *J. Dairy Sci.*, 1957, **40** (11), 1495.—High results in this method (cf. *Brit. Abstr. C*, 1951, 266) are attributed to incomplete pptn. of milk proteins by the 5% trichloroacetic acid. Satisfactory agreement with the gravimetric pentabromoacetone procedure was attained by increasing the trichloroacetic acid concn. to 12%.
W. H. C. SHAW

3155. Procedures for making acidity tests of fluid milk-products. F. J. Doan, B. L. Larson, W. C. Winder and J. G. Leeder (Pennsylvania State Univ., Pa., U.S.A.). *J. Dairy Sci.*, 1957, **40** (12), 1643-1644.—Standard methods recommended by the American Dairy Sci. Assoc. include those for milk, skim-, butter- and condensed milk, whey, cream, ice-cream and chocolate-milk. W. H. C. SHAW

3156. Modification of the method of Saffran and Denstedt for citrate in milk. A. Reinart and J. M. Nesbitt (Manitoba Univ., Winnipeg, Canada). *J. Dairy Sci.*, 1957, **40** (12), 1645-1646.—Improved reproducibility is attained (*J. Biol. Chem.*, 1948, **175**, 849) by reducing the concentration of HCl from 0.1 to 0.05 N. Recovery of added citric acid in milk averaged $98.04 \pm 2.08\%$ and the average variation between replicates was $<1\%$.
W. H. C. SHAW

3157. Determination of the rancidity of melted butter by means of diphenylcarbazide reagent. I. Prekopp (Žilinské Mliekárne, n.p., Žilina, Czechoslovakia). *Průmysl Potravin*, 1957, **8** (11), 596-599.—Various methods were compared and tested experimentally. Although no direct relation between the degree of rancidity and acidity was found, there was a partial dependence between the degree of rancidity and the peroxide number. Thus only oxidation rancidity can be determined by the colorimetric method with the use of diphenylcarbazide reagent.
J. ŽYKA

3158. Detection of exhausted coffee in genuine roasted coffee and estimation of the added amount. Y. Pomeranz (Min. of Trade and Industry, Food Testing Lab., Haifa, Israel). *Anal. Chim. Acta*, 1957, **17** (6), 527-529 (in English).—The sample (10 mg) is uniformly distributed over 3 layers of filter-paper (50 sq. in. in area), each particle is wetted with a drop of boiling water from a dropping pipette, and the paper is examined under u.v. light, preferably in the dark. Genuine coffee particles show a brilliant yellowish fluorescent spot, while steam-exhausted particles do not. The amount of adulterant can be estimated by comparison with known mixtures, or by counting. Better results are given after drying, and no change was observed after storage for several months. Chicory appears

as brownish particles surrounded by a spot of the same colour, while coffee substitutes based on cereals give a brown - yellow fluorescence.

R. E. ESSERY

3159. Calculation of the original extract of beer. M. Brofeldt. *Brauwissenschaft*, 1957, **10** (8), 202-204.—By an extensive series of comparisons of seven different equations used for the calculation of the original extract of beer, it is established that the formulae containing the "apparent" extract value in place of the "real" one yield quite satisfactory results. N. E.

3160. Calculation of the original extract content of the wort in beers. M. Brofeldt. *Brauwissenschaft*, 1957, **10** (12), 313-315.—Results obtained from several formulae are compared. The formula for apparent extract (*cf. Ibid.*, 1957, **10**, 202) gives satisfactory results for bottom-fermented beers, including those made from malt containing at least 10% of substitutes, *viz.* raw grain or sugar. The importance of the removal of CO₂ from the sample for analysis is pointed out. P. S. ARUP

3161. Measurement of enzymic amylolytic activity. Group B. I. Chemical methods. H. Wildner and G. Wildner (Ireks Forschungsinst. für Gärungswissenschaft, Kulmbach, Germany). *Brauwissenschaft*, 1957, **10** (12), 315-317.—Detailed descriptions are given of published methods for the refractometric determination of diastase (in connection with the detection of flour made from wheat damaged by germination), the colorimetric determination of reducing sugars by means of dinitrosalicylic acid (in connection with the determination of amylolytic activity), and methods for the determination of the diastatic activity of honey. P. S. ARUP

3162. Colorimetric determination of sulphur dioxide from malt and beer by complexing with sodium tetrachloromercurate(II). E. B. Beetch and L. I. Oetzel (Res. Dept., Rahr Malting Co., Manitowoc, Wis., U.S.A.). *J. Agric. Food Chem.*, 1957, **5** (12), 951-952.—A rapid, sensitive and specific method is described; the reproducibility is within the range of max. error, *i.e.*, $\pm 5\%$, and recoveries of 98 to 103.6% have been obtained with synthetic SO₂ soln. *Procedure*—Beer (300 g), de-gassed with oxygen-free N for 5 min. and acidified with 20 ml of conc. HCl, is distilled for 45 min. in a stream of N, and the SO₂ is absorbed in 100 ml of sodium tetrachloromercurate^{II} soln. (11.7 g of NaCl and 27.2 g of HgCl₂ in 1 litre of water). A 5-ml aliquot of the distillate is added to 25 ml of bleached rosaniline hydrochloride soln. (30 ml of conc. HCl added to 20 ml of 0.1% aq. soln. of rosaniline in 100 ml of water and when bleached to pale yellowish-green diluted to 500 ml with water) and 2 ml of formaldehyde soln. (5.5 ml of 36% formaldehyde soln. diluted to 100 ml). After 7 min. for colour development, the mixture is diluted to 100 ml and the absorption at 560 m μ is measured immediately. The amount of SO₂ is obtained by reference to a standard curve covering the range 0 to 0.2 mg of SO₂ per 100 ml. For malt, a 50-g sample is diluted with 300 ml of water before carrying out the procedure as described for beer. Results obtained are in close agreement with those of the Monier-Williams gravimetric method. S. C. JOLLY

3163. Spectrophotometric determination of a micro amount of p-ethoxyphenylurea [dulcin]. Masuo Akagi and Setsuzo Tejima (Pharm. Inst., Medical Fac., Hokkaido Univ., Sapporo). *J. Pharm. Soc. Japan*, 1957, **77** (9), 1043-1044.—Jorissen's reaction (*Z. anal. Chem.*, 1896, **35**, 628) of dulcin (I) with Hg(NO₃)₂ was applied to its colorimetric determination. The addition of a small amount of glacial acetic acid (0.5 ml) clarifies the soln. The presence of free HNO₃ in the Hg(NO₃)₂ soln. markedly decreases the sensitivity. Aq. K₂S₂O₈ soln. is the best oxidant. No interference results from aniline, *p*-toluidine, phenacetin, phenol, benzoic acid, *p*-hydroxybenzoic acid, its esters, salicylic acid, urea, saccharin, *p*-nitrophenol, *p*-tolylurea, *p*-hydroxyphenylurea, alanine, phenylalanine and arginine. The sample soln. (4.5 ml) is heated with Hg(NO₃)₂ soln. (2%, 0.5 ml) in a boiling-water bath, then cooled, mixed with K₂S₂O₈ (1%, 0.5 ml), set aside for 1 hr., mixed with acetic acid and measured photometrically at 550 m μ . A standard series (containing <2 mg of I) is prepared similarly and simultaneously. K. SAITO

3164. Chromatographic determination of capsaicin in paprika oil and paprika products. J. Holló, I. Gál and J. Sütő (Inst. for Agric.-chem. Technol., Tech. Univ., Budapest). *Fette, Seif., Anstrichmitt.*, 1957, **59** (12), 1048-1049.—Capsaicin is separated from interfering materials by chromatography on alumina and then determined by absorptiometry of the reaction product with 2:6-dibromo-*p*-benzoquinone-4-chlorimine. *Procedure*—A soln. of paprika oil (1 to 1.5 ml containing 25 mg per ml) in xylene is poured on to a chromatographic column (30 cm \times 1 cm) containing 10 g of Brockmann II alumina, moistened with 10 ml of xylene. The column is developed with xylene under pressure [80 to 100 mm (Hg)] of an inert gas until the eluate is colourless. The capsaicin is then eluted with 20 ml of CHCl₃. The CHCl₃ soln. is evaporated to 5 ml and transferred to a separator with 30 ml of light petroleum. The soln. is extracted first with 10 ml of 0.1 N NaOH and then with 10 ml of water. The combined aq. extracts are neutralised with 0.1 N HCl and made up to 100 ml with water. To a 10-ml aliquot are added 3 ml of Thériault buffer and 1.0 mg of 2:6-dibromo-*p*-benzoquinone-4-chlorimine (in ethanolic soln.). The vol. is made up to 50 ml and the soln. is set aside for 30 min. The intensity of the colour is measured in a Pulfrich photometer, and the capsaicin content is determined from a calibration curve. The method is suitable only for samples of paprika with a high capsaicin content or for oleoresin of paprika. E. HAYES

3165. Determination of capsaicin. I. Reaction of capsaicin with diazotised sulphanilic acid. V. Zitko (Dept. of Glycides and Biochemistry, Acad. Sci., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1957, **11** (10), 590-599.—The conditions for the coupling of diazotised sulphanilic acid with capsaicin (suitable medium, influence of ethanol, distillation conditions, influence of pH) were studied. The use of borate instead of glycine buffer soln. enables higher extinction coeff. to be obtained. Ethanol decreases the sensitivity of the reaction and must be removed by distillation in nitrogen. J. ŽYKA

3166. Paper chromatography of permitted and prohibited colours in foodstuffs. J. Moreno Calvo (Biochem. Dept., Inst. Español de Fisiol. y Bioquím.). *An. Bromatol.*, 1957, **9** (4), 423-445.—A

scheme for the identification of 45 commonly used food colours is presented with diagrams and tabulated R_F values. The colour is extracted from the dried and ground foodstuff with amyl alcohol, ether, ethanol or water, and the soln. is evaporated to $\approx 1\%$ of dry matter. From 1 to 2 μ l is applied to a Whatman No. 1 paper and developed for 21.5 hr. with ethyl acetate-pyridine-water at $20^\circ \pm 0.5^\circ$ according to the technique previously described (*Anal. Abstr.*, 1956, **3**, 837). The colours are identified on the basis of their characteristic R_F values, together with the character of the colour shown by the developed spots when observed in visible and in u.v. light. The minimum quantity of dyestuff necessary for identification is from 0.001 to 0.01 mg. E. C. APLING

3167. Separation and identification of fatty acids. XXII. Quantitative analysis of fatty acids by paper chromatography. Yoshiyuki Inoue, Osamu Hirayama and Manjiro Noda (College of Agric., Kyoto Univ., Sakyo-ku, Kyoto). *J. Agric. Chem. Soc. Japan*, 1957, **31** (8), 568-572.—Saturated (C_4 to C_{22}) and unsaturated (oleic acid series, C_{18} to C_{22}) fatty acids are converted into their *p*-bromophenacyl bromide 2:4-diphenylhydrazones by refluxing the neutralised acid (20 mg) with *p*-bromophenacyl bromide (equiv. amount) in ethanol (1 ml), followed by treatment with a slight excess of 2:4-dinitrophenylhydrazine (0.5%), in 2 N HCl in methanol. The benzene extract (1 ml) is subjected to paper chromatography (*Bull. Agric. Chem. Soc. Japan*, 1956, **20**, 200, in English), with light petroleum (boiling range 140° to 170°) as stationary phase and a mixture of methanol, acetic acid and the light petroleum (5 + 1 + 1, by vol.) as developer at 30° for 5 hr. The yellow spots are separately extracted with benzene (5 ml) and the extinction is measured at $375 m\mu$. All fatty acids of the same series give approx. identical absorption curves. The overall error is $< 3\%$. K. SAITO

3168. Separation and identification of saturated and unsaturated fatty acids from formic to C_{20} by means of gas-liquid chromatography. A. T. James (Nat. Inst. Med. Res., London). *Olii Min.*, 1957, **34** (12), 539-543.—The analysis of fatty acids by gas-liquid chromatography is described, with numerous examples and some tables of retention volumes of methyl esters with various stationary phases. L. A. O'NEILL

3169. Single versus duplicate determinations for the estimation of vitamin A and tocopherol in calf livers. M. W. Dicks, J. E. Rousseau, H. D. Eaton, R. Teichman and H. L. Lucas (Storrs Agric. Exp. Sta., Conn., U.S.A.). *J. Dairy Sci.*, 1957, **40** (11), 1492-1494.—From a statistical examination of results for vitamin A (two methods) and tocopherol (one method) it is concluded that single determinations are adequate in treatment studies, but random samples should be assayed in duplicate and the results applied to the control chart given in order to detect assay errors. W. H. C. SHAW

3170. Polarography and oscillography of vitamin B₁ from the analytical standpoint. R. Pleticha (Res. Inst. for Plant Prod., Prague). *Anal. Chim. Acta*, 1958, **18** (1-2), 146-154 (in German).—Electro-active substances derived from thiamine and cocarboxylase are studied oscillographically, thereby opening up the possibility for the non-enzymic determination of vitamin B₁ in natural material. J. H. WATON

3171. Determination of flavins. K. Yagi (Inst. de Biol. Phys.-Chim. et C.N.R.S., Paris). *Bull. Soc. Chim. France*, 1957, (11-12), 1543-1550.—A review is presented of methods of determining flavins, particularly riboflavin, flavin mononucleotide, and flavinadenine dinucleotide. Total flavins are best determined by photodecomposition to lumiflavin and determination in a fluorimeter. The effect of time of irradiation, and temp. and pH of the soln. on the content of lumiflavin is discussed. To determine the separate flavins, paper-chromatographic and electrophoretic methods are detailed, together with a method for determining the fluorescence directly on the paper. (59 references.) E. J. H. BIRCH

3172. Quantitative determination of nicotinamide in the presence of nicotinic acid. B. P. Lisboa (Tuberkulose-Forschungsinst., Borstel, Germany). *Naturwissenschaften*, 1957, **44** (23), 617-618.—The advantage claimed for this method over others is that nicotinamide is measured directly and that the determination is independent of the concn. of nicotinic acid. Nicotinamide is coupled with barbituric acid in the presence of cyanogen bromide as follows. The mixture of nicotinamide and nicotinic acid is dissolved in 3 ml of phosphate buffer ($M/15$, pH 7.2), to which are then added 1 ml of 1% aq. barbituric acid soln. and 1 ml of 10% aq. cyanogen bromide. The mixture is kept for 30 min. at 20° to 22° , and the extinction of the soln. is then read in a spectrophotometer at $513 m\mu$, at which nicotinic acid shows no extinction. The method is sensitive down to $\approx 3 \mu g$ per ml. E. KAWERAU

See also Abstracts—3018, Infra-red identification of disaccharides. 3050, Determination of Cu in gelatin. 3079, Determination of urinary excretion of vitamin B₁₂. 3147, Determination of capsaicin. 3191, Determination of pesticide residues on cherries. 3192, Determination of Karathane in food crops.

Sanitation

3173. Interpretation of mass spectra of condensates from urban atmospheres. E. R. Weaver, E. E. Hughes, S. M. Gunther, S. Schuhmann, N. T. Redfearn and R. Gorden, jun. (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *J. Res. Nat. Bur. Stand.*, 1957, **59** (6), 383-404.—Resolution into separate components of the complex mixtures in condensates (at -183°) of urban atmospheres is not possible by mass spectrometry even when a multiple distillation of the sample into 50 fractions is made. The number of chemical compounds is far in excess of the number of masses recorded from > 80 usable peaks. By assuming approx. const. composition of each source, viz. traffic gases, local smog, chemical plants, many sources can be identified and their contribution to the total pollution determined approx. Application of this procedure to condensates from seven cities in east and west U.S.A. is described fully. Acetylene, ethanol, benzene, toluene and equimol.-wt. groups of heavier aromatic hydrocarbons can be determined and removed from the spectrum as separate compounds. Mass-spectral patterns for normal and

oxidised traffic gas can also be removed to facilitate recognition and determination of other main pollutants. The compounds characterising 12 different pollutant sources are listed.

W. J. BAKER

3174. Ionophoretic and chromatographic analysis of single dust particles. B. M. Turner (Turner Lighter Spares and Components, Ltd., Burroughs Hse., Hendon Central, London). *Nature*, 1957, **180**, 1472-1473.—The particles are treated by the "breath figure" procedure previously described (*Anal. Abstr.*, 1957, **4**, 3811), on a clean glass surface in a moist chamber. Each particle forms a hydrophobic or hydrophilic halo of contamination up to 1 mm in diameter. This can be further developed by condensing a film of water or acid 0.1 to 10 μ thick on the glass, allowing to stand for 1 to 10 min. in the chamber, neutralising with NH_3 if necessary, and drying. Concentric rings may be formed, corresponding to circular chromatographic development on paper, and increased by repeatedly condensing and evaporating the film. Unknown particles could possibly be identified by comparison with results from dusts of known composition.

R. E. ESSERY

3175. Field method for the rapid determination of hydrogen cyanide in air. B. E. Dixon, G. C. Hands and A. F. F. Bartlett (Dept. Gov. Chem., Clement's Inn Passage, Strand, London). *Analyst*, 1958, **83**, 199-202.—The test is based on the formation of Prussian blue on test paper impregnated with FeSO_4 and NaOH . The sheet of filter-paper (Whatman No. 50, 4 in. \times 3 in.) is immersed in 10% FeSO_4 soln., dried and, after the discarding of a 2-in. strip of the lower edge, is cut into strips (3.5 cm \times 2.5 cm) which are immersed singly in 20% carbonate-free NaOH soln. and dried in a vacuum-desiccator. Each strip is stored in a glass tube sealed under vacuum (absence of CO_2 and O is essential). In use, the strip is clamped between inlet and outlet tubes and the sample of air (360 ml at 6 ml per sec.) is drawn through by means of a rubber-bulb hand aspirator. The paper is immersed in 30% H_2SO_4 and the blue stain is compared with standard stains. The test is specific for HCN and there is no interference from HCl and NH_3 in concn. up to 400 p.p.m. The test is sensitive to slightly less than 1 p.p.m. of HCN in air.

A. O. JONES

3176. New method of detection and determination of chlorinated ethylenic solvents in air. A. Berton. *Compt. Rend.*, 1957, **245** (16), 1317-1318.—The method, which is specific, depends on the conversion of dichloroethylene, trichloroethylene and tetrachloroethylene by u.v. light into phosgene and chloroacetyl chlorides. The air (e.g., in workshops) is aspirated by a micro-pump into a container illuminated by a low-pressure, mercury-vapour lamp and is then directed against a filter-paper impregnated with *p*-dimethylaminobenzaldehyde and dimethylaniline. The paper becomes yellow changing to blue, the intensity of which increases with solvent concn. Since the micro-pump has const. discharge, the concn. of solvent can be calculated from the time needed to obtain a standard tint. The sensitivity of the apparatus is 0.1 mg of trichloroethylene or tetrachloroethylene per litre of air.

W. J. BAKER

3177. Determination of thiophosphoryl chloride in the atmosphere. V. Kratochvil and J. Langner (Res. Inst. Org. Syntheses, Pardubice-Rybitvi). *Pracovní Lékařství*, 1957, **9** (1), 54-56.—The air to be analysed (2 to 10 litres) was drawn in through two traps filled with 2 *N* NaOH (10 ml each) heated to between 50° and 60°, at 40 to 50 litres per min. The contents of the traps were analysed colorimetrically by means of the modified Roth method for the determination of phosphorus (formation of molybdenum blue after reduction of ammonium molybdophosphate in slightly acidic medium with metol). Sodium sulphite interferes and has to be removed by oxidation with KMnO_4 . J. VOLKE

3178. Photometric determination of colour and turbidity of water with proposed new standard definitions. A. T. Palin (Newcastle - Gateshead Water Co., Newcastle upon Tyne, England). *Wat. & Sewage Wks*, 1957, **104** (11), 492-495.—The proposed standard definitions are—the unit of turbidity is to be taken as that of a suspension having an optical density of 0.001 per cm depth to yellow light of peak wavelength 580 $\text{m}\mu$; the unit of colour is to be taken as that of a clear water having an optical density of 0.001 per cm depth to violet light of peak wavelength 425 $\text{m}\mu$. The optical density of the sample is determined with Ilford filters 601 and 606, the colour readings are corrected for turbidity effects, and the turbidity values are corrected for colour, by using a nomogram, the construction of which is described. J. M. JACOBS

3179. The Winkler method for dissolved oxygen determination. V. S. Griffiths and M. I. Jackman (Chem. Dept., Battersea Polytechnic, London). *Anal. Chim. Acta*, 1957, **17** (6), 603-605 (in English).—An improved final iodine titration in the Winkler method is carried out potentiometrically with $\text{Na}_2\text{S}_2\text{O}_3$ soln., with magnetic stirring. A variable-speed titration unit is used, with a glass electrode as reference electrode and a platinum spiral as indicator electrode, the potential being measured with a pH - mV meter connected to a chart recorder. The increase rate of change of potential at the end-point is used to switch off the titration unit (Malmstadt and Fett, *Anal. Abstr.*, 1954, **1**, 3185; 1956, **3**, 1214; Audran and Dighton, *Anal. Abstr.*, 1956, **3**, 2941). With lithium glass electrodes, the end-point potential (211 mV) was independent of the electrode used, and its reproducibility was good over the range 0.4 to 4.4 p.p.m. of oxygen.

R. E. ESSERY

3180. Wide-bore dropping mercury electrode and its application for automatic recording of dissolved oxygen. G. Knowles, R. Briggs and G. V. Dyke (Water Pollution Res. Lab., Stevenage, Herts., England). *J. Polarographic Soc.*, 1958, **1** (1), 17-20.—A special type of cell for use with a wide-bore (0.8 mm) electrode, and a system for the supply of mercury to the electrode are described. The method is designed to give a stable calibration for field expt. Dissolved O in water is determined with a standard deviation of ± 0.06 p.p.m.

H. F. W. KIRKPATRICK

3181. The determination of the oxidisability of natural waters. R. Buydens and R. Ledent (Lab. de la Comp. Intercommun. Bruxelloise des Eaux). *Bull. Centre Belge Étude et Document. Eaux*, 1957, (38), 238-241.—The following procedures are

examined critically for their reliability—(i) 10-min. boil with acidified 0.01 *N* KMnO_4 , (ii) 20-min. heating under reflux with 25 ml of 0.01 *N* $\text{Ce}(\text{SO}_4)_2$, and (iii) 2-hr. heating under reflux with 0.25 *N* $\text{K}_2\text{Cr}_2\text{O}_7$. Approx. the same values are obtained with the KMnO_4 and $\text{Ce}(\text{SO}_4)_2$ methods provided that the KMnO_4 soln. is kept free from MnO_2 . Higher values are found if the stated boiling period or vol. of oxidant is exceeded. The $\text{K}_2\text{Cr}_2\text{O}_7$ method gives much higher values than do the other two methods, mainly because the reagent attacks a greater number of reducing substances in the sample. Because of the non-uniform oxidation of the AgCl ppt. it is recommended that the Ag_2SO_4 (often added as catalyst) be omitted always. If 0.05 *N* $\text{K}_2\text{Cr}_2\text{O}_7$ is used there may be incomplete oxidation of Cl^- within 2 hr. As oxidant, KMnO_4 is preferred to $\text{Ce}(\text{SO}_4)_2$.

W. J. BAKER

3182. Volumetric determination of fluorine in natural waters. S. K. Chirkov (A.M. Gorky Ural State Univ.). *Zhur. Anal. Khim.*, 1957, **12** (6), 762-763.—A modification of the $\text{Th}(\text{NO}_3)_4$ -alizarin red S method is described. The optimum acidity for the titration is at pH 2.0 to 2.3, and CaCl_2 is added to suppress the interference of SO_4^{2-} .

G. S. SMITH

3183. The turbidimetric micro-determination of phosphorus applied to waters containing polymetaphosphates. (II). G. van Beneden (Cébedeau, 2 rue Arm. Stévant, Liège, Belgium). *Bull. Centre Belge Étude et Document. Eaux*, 1957, (38), 254-260.—The formation of a strychnine-molybdophosphoric complex is 10 times as sensitive a test for P than is the classical molybdophosphate test. The turbidity produced is proportional to concn. of P, and Beer's law is followed between 1 and 12 μg of P in a vol. of 11.2 ml. The lower limit of detection is 1 μg of P, and the reaction can be used to determine the amount of added hexametaphosphate (I) in water; if the concn. of I is ≤ 1 mg per litre, the sample need not be concentrated. There is no interference from SiO_2 , but PO_3^{2-} must be converted into PO_4^{3-} by refluxing for 10 min. with concn. HNO_3 (1.5 ml). *Procedure*—To the sample (diluted if necessary) add 1% aq. strychnine sulphate (0.5 ml), concn. HNO_3 (0.5 ml), HNO_3 -ammonium molybdate reagent (0.2 ml) and H_2O to make the final vol. 10.2 ml. Mix well and, when the turbidity has developed (10 min.), add 1% aq. carboxymethyl-cellulose soln. (1 ml). Shake well and wait ≈ 30 min. before measuring the percentage transmission of the soln. spectrophotometrically at 420 $m\mu$ in a 14-mm cell. The quinine- and phenazone-molybdophosphoric complexes may be adapted to a similar procedure.

W. J. BAKER

3184. Quantitative determination of strontium-89 and strontium-90 in water. J. Kooi (Radiochem. Group, Reactor Centrum Nederland, The Hague, The Netherlands). *Anal. Chem.*, 1958, **30** (4, Part I), 532-535.—The method described is specific for Sr and suitable for large-scale routine application. The procedure has 3 principal stages—(i) concentration, (ii) separation and purification of the total Sr, (iii) determination of total Sr activity and determination of ^{89}Sr separately. The sensitivity is better than one-tenth of the internationally recommended max. permissible concn. K. A. PROCTOR

3185. Rapid spectrophotometric method for determination of a minute amount of vanadium in natural waters. Hideo Naitō and Ken Sugawara (Chem. Dept., Nagoya Univ., Chikusa Nagoya, Japan). *Bull. Chem. Soc. Japan*, 1957, **30** (7), 799-800 (in English).—The method of separating V from Fe and Al after co-pptn. of the oxides has been improved.

The sample (5 to 20 litres) is acidified with HCl and treated with enough aq. FeCl_3 or other ferric salt, to give 10 mg of Fe per litre. The warm soln. is neutralised to bromocresol purple with 4 *N* aq. NH_3 and the ppt. is filtered off and ashed in a platinum dish. The ash is dissolved in 5 ml of 6 *N* HCl, washed into a beaker with 50 ml of water, treated, with stirring, with 15 ml of a soln. of 30 g of tartaric acid and 200 g of NaOH in 1 litre of water, and heated on a steam bath until $\text{Fe}(\text{OH})_3$ is completely pptd. (30 min.). The cooled soln. is made up to 100 ml and centrifuged for 10 min., then 80 ml of supernatant liquor is neutralised to *p*-nitrophenol with 4 *N* H_2SO_4 and a 3-ml excess of acid is added. The hot soln. is treated with 2 ml of oxine soln. (2 g of oxine and 5 g of malonic acid per 100 ml), neutralised with 4 *N* aq. NH_3 and treated with 4 ml in excess. Any trace of Fe left is pptd. as oxinate and may be centrifuged off if necessary, but it is normally adequate to remove interfering oxinates by extraction with benzene (2×20 ml). The remaining soln. is neutralised with 4 *N* H_2SO_4 , adding 3 ml in excess, and the pH is adjusted to 4 with Na acetate buffer. Oxine soln. (1 ml) is added and the V oxinate is extracted with pentanol, made up to 10 ml, and determined spectrophotometrically at 475 $m\mu$. The recovery is $100 \pm 4\%$ for 20 mg of V. Small concn. of other metals do not interfere.

A. B. DENSHAM

3186. Recommended methods for the analysis of trade effluents. Methods for the determination of residual chlorine, cyanides and thiocyanate, fluoride, formaldehyde, and sulphite and thiosulphate. The Joint A.B.C.M. - S.A.C. Committee on Methods for the Analysis of Trade Effluents. *Analyst*, 1958, **83**, 230-241.—For residual Cl (up to 1 mg per litre), the colour developed with *o*-tolidine is measured visually or spectrophotometrically at 435 $m\mu$. Interfering elements are determined by preliminary removal of the Cl with sodium arsenite. For higher contents (1 to 10 mg per litre), iodine liberated from KI is titrated with 0.005 *N* $\text{Na}_2\text{S}_2\text{O}_3$. Total cyanide (including complex cyanides yielding HCN) is determined by distillation with CuCl_2 , collection of the distillate in dil. NaOH and titration with AgNO_3 , *p*-dimethylaminobenzylidinerhodanine soln. (0.02% in acetone) being used as indicator. To exclude $\text{Fe}(\text{CN})_6^{4-}$, the neutralised sample is distilled with Pb acetate, the CN^- are determined as before and then $\text{Fe}(\text{CN})_6^{4-}$ are determined by re-distillation with acid CuCl_2 soln. By Aldridge's method CN^- and SCN^- are converted into CNBr, which is then determined visually or spectrophotometrically at 520 $m\mu$ as the red compound formed by coupling it with benzidine in pyridine soln. For SCN^- , FeCl_3 is added directly to the sample and the colour is compared with that of standards. Fluoride is determined (after destruction of organic matter by heating with CaO and removal of free Cl by arsenite) by steam-distillation as fluosilicic acid in the presence of HClO_4 , and measuring by titration the bleaching action of F^- on the thorium lake of alizarin red S. Formaldehyde is determined by reaction with acetylacetone in the presence of excess of ammonium salt to form yellow diacetylhydrolutidine, which is measured spectrophotometrically

at 425 m μ . To determine sulphite and thiosulphate, the total iodine equiv. is determined and then the S₂O₃²⁻ iodine equiv. by masking the SO₃²⁻ with formaldehyde.

A. O. JONES

See also Abstracts—2887, Determination of Na in water. 2987, Concentration of Fe from natural waters. 3225, Measurement of SO₂ in air.

Agriculture and Plant Biochemistry

3187. Detection of flavanones by reduction with sodium borohydride. R. M. Horowitz (U.S. Dept. of Agric., Pasadena, Calif.). *J. Org. Chem.*, 1957, 22 (12), 1733-1735.—Reduction with sodium borohydride in ethanol, either in soln. or on paper chromatograms, may be applied to the detection of most naturally occurring flavanones since the 4-hydroxyflavones formed give a brilliant purple or blue-red colour on treatment with strong acids. Chalcones, flavones, flavonols, isoflavones and aurones are not reduced with sodium borohydride and do not give the characteristic colour. N. E.

3188. Spectrophotometric methods for determining pigmentation— β -carotene and lycopene—in Ruby Red grapefruit. B. J. Lime, F. P. Griffiths, R. T. O'Connor, D. C. Heinzelman and E. R. McCall (U.S. Fruit and Veg. Prod. Lab., S. Utilization Res. and Develop. Div., U.S. Dept. of Agric., Weslaco, Tex., U.S.A.). *J. Agric. Food Chem.*, 1957, 5 (12), 941-944.—Two methods are described. One is a relatively rapid chromatographic method for determining carotene and lycopene extracted from the juice, separated solids and pulp. The hexane-extracted pigments are separated by adsorption on a column of magnesia-Super Cel, followed by differential elution. The carotene is determined from the extinction at 451 m μ of one eluate, and lycopene from the extinction at 471 m μ of another eluate. Recovery of pigments after chromatographing averaged 97.5% for carotene and 95.4% for lycopene. Analyses are correct, in mg per 100 g of sample, within ± 0.013 mg for carotene and ± 0.012 mg for lycopene ($P = 0.05$). The second method is more rapid, but gives results which are 10 to 15% higher than those by the first method. Chromatographic separation of the pigments is omitted, and the hexane extract of the pigments is examined spectrophotometrically directly; carotene and lycopene are reported as total pigments, calculated from absorptions at 451 and 503 m μ .

S. C. JOLLY

3189. Quantitative estimation of the resistance factor, 6-methoxybenzoxazolone, in corn plant tissue. S. D. Beck, E. T. Kaske and E. E. Smismann (Dept. of Entomology and Pharm. Chem., Univ. of Wisconsin, Madison 6, U.S.A.). *J. Agric. Food Chem.*, 1957, 5 (12), 933-935.—The plant tissue (>1 g fresh wt.), previously frozen and, if necessary, dried at $>50^\circ$, is extracted with ether for 3 hr. in a micro-Soxhlet apparatus, the solvent is removed from the extract at room temp., and the residue is purified by dissolving in 5-0 ml of anhyd. ether and chromatographing on a column (10 in. \times 26 mm) of alumina [prepared by slurring 100 g in 200 ml of

dehydrated ethanol and then washing the column with <450 ml of anhyd. ether-anhyd. ethanol (4:1, by vol.)]. Ether (3 \times 3 ml) is used to transfer the extract to the column, followed by 10 ml of the ether-ethanol mixture. The chromatogram is developed with the solvent mixture, and, after discarding the first 90 ml of eluate, 6-methoxybenzoxazolone (resistance factor A) is determined in the next 200 ml by evaporating the eluate to dryness at $>40^\circ$, dissolving the residue in 10 ml of water, with warming, and measuring the absorption at 255 and 285 m μ , against water as a blank. The concn. of factor A is determined by reference to the absorption of pure recrystallised 6-methoxybenzoxazolone. With pure soln. as little as 2 μ g of factor A can be determined.

S. C. JOLLY

3190. Determinations of molecular weight of lignin degradation products by three methods. S. K. Gross, K. Sarkanen and C. Schuerch (Syracuse Univ., N.Y., U.S.A.). *Anal. Chem.*, 1958, 30 (4, Part I), 518-520.—An isopiestic method with tetrahydrofuran as solvent and cryoscopic methods with dioxan and ethylene carbonate (the cyclic carbonate of ethanediol) as solvents were applied to lignins. Special techniques were used to eliminate errors due to ash content and adsorbed solvents. Cryoscopy in ethylene carbonate gave the most reproducible results. When dioxan was used, dependence of mol. wt. on concn. indicated excessive association, and erratic results with tetrahydrofuran were probably due to the same cause.

G. P. COOK

3191. Determination of residues of OO-dimethyl S-methylcarbamylmethyl phosphorodithioate on cherries treated with it and products based on such insecticides. R. Santi and B. Bazzi (Lab. Sperimentale Agrario, Signa, Firenze). *Chimica, Milano*, 1956, 12, 325-328.—Laboratory and field studies have shown the efficacy of this insecticide against *Rhagoletis cerasi* L., and means of determining the amount of residue present on harvested fruit have been investigated. Two methods are described—(a) colorimetric, and (b) chromatographic. The colorimetric method is based on the extraction of the insecticide from the ground cherries with CHCl₃-methyl cyanide (9:1), followed by hydrolysis to methylamine, treatment with ninhydrin to give NH₃ and formaldehyde, and photometric determination of the formaldehyde with chromotropic acid (cf. Bazzi *et al.*, *Anal. Abstr.*, 1957, 4, 2830). For the chromatographic method, the extract is purified by treatment with activated earth before application to S. & S. paper 2045b. The ascending technique is used, with CCl₄-methanol-nitromethane (90:5:5) as developer and HClO₄-N HCl-4% ammonium molybdate soln. (4.5:10:25) for revealing the spots. The colorimetric method is claimed to have a sensitivity of 0.02 p.p.m., whilst the chromatographic method has a precision of 0.6 p.p.m. The colorimetric method, in addition to greater sensitivity, has the further advantage of taking less time and being, in general, simpler to carry out.

J. F. P. H. GREENE

3192. Micro-determination of the fungicide dinitrocaprylphenyl crotonate [2-(1-methylheptyl)-4:6-dinitrophenyl crotonate] [Karathane] in food crops and animal tissues. I. Rosenthal, C. F. Gordon, E. L. Stanley and M. H. Perlman (Rohm & Haas Co.,

5000 Richmond St., Philadelphia 37, Pa., U.S.A.). *J. Agric. Food Chem.*, 1957, **5** (12), 914-918.—The method described for the determination of 2-(1-methylheptyl)-4:6-dinitrophenyl crotonate residues and its decomposition product methylheptyl-dinitrophenol had a coeff. of variation of $\pm 7.7\%$ at the 40- μg level and $\pm 8.7\%$ at the 20- μg level in a 200-g fruit or vegetable sample. Recoveries from a 200-g sample extract averaged 55 to 100% of that obtained in the absence of substrate (83% of the theoretical recovery). *Procedure*—The solvent is removed from an aliquot of plant extract in benzene containing $>130\ \mu\text{g}$ of fungicide, and after adding 15 ml of H_2SO_4 (50% v/v) the residue is steam-distilled so that 800 ml of distillate is collected in 1 hr. The distillate is transferred to a separating funnel with 10 ml of ethanol (95%) and two 50-ml portions of CHCl_3 . After shaking for 2 min. and allowing to separate, the CHCl_3 layer is evaporated to dryness and 3 ml of pyridine-water reagent (1:1, by vol.) is added to the residue. After 1 hr., with occasional swirling, the absorption of the yellow soln. at 442 μm is measured against a reagent blank. The amount of fungicide is obtained by reference to a calibration curve prepared by treating aliquots of a standard soln. of 2-(1-methylheptyl)-4:6-dinitrophenyl crotonate by a similar procedure. Determination of the fungicide in animal tissue requires a special extraction method.

S. C. JOLLY

See also Abstracts—3023, Chromatography of volatile aliphatic acids. 3024, Chromatography of non-volatile organic acids. 3086, Chromatographic determination of carbohydrates. 3216, Spectrophotometric examination of leaves.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

3193. Weighing method for small amounts of hygroscopic and volatile liquids. W. J. Schuele and W. M. McNabb (Univ. of Pennsylvania, Philadelphia, U.S.A.). *Chemist Analyst*, 1957, **46** (4), 101.—The liquid, followed by a bubble of inert gas, is drawn into a 1-ml tuberculin syringe. The syringe is then used as a weight burette. The usual precautions for semi-micro work are taken.

G. S. ROBERTS

3194. Production of large amounts of pure water. K. T. Marvin and L. M. Lansford (U.S. Fish and Wildlife Service, Galveston, Tex., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 551-552.—The construction and operation of two all-glass stills that produce daily >50 gal. of high-purity H_2O are described and illustrated. Both stills operate at 220 V, one using 70 amp. to produce ≈ 5 gal. per hr. of H_2O having sp. conductance $\approx 1.3 \times 10^{-6}$ mho, and the other (fed with distillate from the first) using 40 amp. to yield ≈ 2.5 gal. per hr. of H_2O having sp. conductivity $\approx 0.7 \times 10^{-6}$ mho. The twice-distilled H_2O is used for the prep. of nutrient soln. and for trace-element analyses.

W. J. BAKER

3195. Micro-analytical investigations in iron research. III. Handling of microgram quantities in metal investigations. W. Koch, H. Malissa and D. Ditzges (Max-Planck-Inst. für Eisenforschung, Düsseldorf). *Arch. Eisenhüttenw.*, 1957, **28**, 785-794.—A micro-manipulator is described for mechanical and chemical work on micro samples. Sampling by drilling and electrolysis, preparation of etching surfaces, and mechanical and magnetic separations are discussed. Analytical investigations can be carried out by fusion, with a platinum wire with borax or sodium peroxide as fusing substance, and by titration. A micro-burette is described with a capacity of 10^{-6} litre and an accuracy of 8×10^{-6} litre. H. SAWISTOWSKI

3196. Oxidimetric and reductimetric titrations in neutral solutions. (Application of sodium triphosphate as masking agent to volumetric analysis.) Susumu Suzuki, Kenji Harimaya, Morio Ueno, Nobuo Tsuji and Noriko Yamaoka (Inst. Chem., Kinki Univ., Fuse, Osaka, Japan). *Bull. Chem. Soc. Japan*, 1957, **30** (7), 766-770 (in English).—Various oxidimetric and reductimetric titrations can be carried out in neutral soln. in the presence of $\text{Na}_3\text{P}_3\text{O}_{10}$. Thus, Sb^{3+} , As^{3+} , Cr^{3+} , Fe^{2+} , Mo^{5+} , Se^{4+} , Ti^+ , Ti^{2+} and V^{4+} can be titrated with chromate (catheline as indicator), bromate (amaranth as indicator), hypobromite, permanganate (crystal violet as indicator), and vanadate. Reductimetric titrations of Ce^{4+} , hypobromite, chromate, triiodide, permanganate, vanadate and H_2O_2 can be carried out with Cr^{3+} , Fe^{2+} , Ti^{3+} and vanadyl soln. The accuracy of the titrations is within $\pm 1\%$.

A. B. DENSHAM

3197. Applications of adsorption micro-chromatography on thin layers. E. Demole (Inst. de Biol. Phys.-chim., Paris). *J. Chromatography*, 1958, **1** (1), 24-34 (in French).—A review is presented, with 29 references, in which the use of "chromatostrips" (cf. Kirchner *et al.*, *Brit. Abstr. C*, 1951, 316) is discussed. These are strips of glass, $12\text{ cm} \times 1.2\text{ cm}$, coated on one side with a layer of adsorbent, water and a binding agent such as starch, which, when dry, is 0.5 mm thick. The ascending technique is used, and the capillary rise of the solvent achieves the separation in about 30 min. by a process of true adsorption. "Chromatoplates" (Reitsemma, cf. *Anal. Abstr.*, 1954, **1**, 2469) are large chromatostrips, $17\text{ cm} \times 11\text{ cm} \times 0.2\text{ cm}$, on which several separations can be run simultaneously, R_F values being then rigorously comparable owing to the great regularity of distribution of the adsorbent. R_F values on chromatostrips are reproducible to about ± 0.5 . Water-soluble substances, easily separable on paper by the partition mechanism, are not suitable for the true adsorption mechanism of chromatostrips, and the reverse is true of fat-soluble substances. Suitable adsorbents, solvents and methods of detection of the spots are discussed, with details of the preparation and manipulation of chromatoplates coated with silicic acid and starch; their use for microchemical reactions and for preparative and micro-preparative work is discussed.

R. E. ESSERY

3198. Electrostatic discharge method of zone location for paper chromatographs. I. G. G. Blake (Sydney Univ., Australia). *Anal. Chim. Acta*, 1957, **17** (5), 489-491 (in English).—A conducting layer (aluminium paint) is satisfactory on

the outside of an electric lamp forms an electron source sufficient to maintain a charge on an electro-scope. Paper chromatograms passed between suitably connected contacts discharge the electro-scope when a conducting zone reaches the contacts. A neon lamp can be used in place of the electro-scope.

II. G. G. Blake. *Ibid.*, 1957, **17** (5), 492-493.—If a paper chromatogram is passed between a pair of contacts connected, respectively, to earth and to the grid of a triode valve, conducting zones can be detected by means of a meter in the anode circuit.

G. BURGER

3199. Simple depositors for paper chromatography. J.-P. DuRuisseau (National Cancer Inst., Bethesda, Md., U.S.A.). *Anal. Chem.*, 1958, **30** (3), 455-456.—Two devices, one hand-operated (for vol. of 10 to 100 μ l) and one automatic (for larger vol.), are described for transferring quant. the solution of a previously dried extract from an evaporating dish to a paper chromatogram. Both devices are based on forced-flow applicators where the rate of flow can be controlled.

K. A. PROCTOR

3200. Reservoir for paper chromatography for use inside a rectangular glass container. A. L. Sims (Univ. of Wales, Cardiff). *J. Sci. Instrum.*, 1957, **34** (11), 461.—A polyethylene rod (diam. 2 in.), long enough to fit between the opposite walls of the container, is provided with holes (0.5 in. diam.) at intervals along its length, these being connected by slots (0.125 in. wide) which hold the paper without clips.

G. SKIRROW

3201. Two-dimensional chromatography on a rotating paper disc. H. J. McDonald and L. V. McKendell (Grad. Sch. and Stritch Sch. of Med., Loyola Univ., Chicago, Ill., U.S.A.). *Naturwissenschaften*, 1957, **44** (23), 616-617.—The substance is chromatographed by a one-dimensional technique on a circular disc of 30 cm diam. with the aid of centrifugal force, which gives satisfactory separation over this distance in a period of 5 to 10 min. The spots do not open out to form arcs under these conditions, but remain as circular or oblong areas resembling one-dimensional separations on ordinary paper strips. After the first separation, the paper disc is cut into two halves at right angles to the trail of separated material. The two halves are stapled together in such a way that the second solvent now moves at right angles to the first (diagram shown) giving rise to a two-dimensional chromatogram. The whole procedure takes ≈ 20 minutes.

E. KAWERAU

3202. Inorganic paper chromatography. V. Relation between the R_F value and the amount of hydrochloric acid - butanol developer used in the ascending and the descending method. Syoichi Yamada (Fac. of Sci., Mie Univ., Tsu). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (7), 1006-1009.—The amount of developer (butanol containing various amounts of N HCl) was measured for the chromatography of Cu, Cd, Bi and Hg by the ascending and the descending methods. In the latter method, more developer flows and the R_F value is greater. There is linear relationship between the amount of developer flow and the distance of migration. When the R value (ratio of the migration distance to the amount of flow; generally used in column chromatography)

is introduced instead of the R_F value, good agreement was observed between results obtained by the two methods.

K. SAITO

3203. Separation of isotopes by chromatography and electrophoresis. M. Chémia (Phys. et Chim. Nucléaires, Collège de France, Paris). *J. Chromatography*, 1958, **1** (1), 2-23 (in French).—A review is presented, with 45 references, in which the following chromatographic and electrophoretic techniques are discussed—ion-exchange chromatography on synthetic zeolite or resin columns (for isotopes of Li and Na, and of N in the form of ammonium salts), and fractional adsorption chromatography in the gaseous phase on activated carbon at the temp. of liquid air or N (for Ne), and on palladium black - asbestos at ordinary temp. (for H). Electrophoretic techniques include migration of a zone of two isotopes, migration in monocrystals at high temp. (for Na), in aq. soln. in agar gels or on paper (for Li and Na), and in fused salts on asbestos paper (for Na, Li, Rb and Cs), counter-current migration in aq. soln. (for K, Cu, Cl and U), and in fused salts (for Li, Cl, Zn, Ag, Cu and Pb). Diagrams of the apparatus are given, and the theory of the various methods, and the factors governing the degree of separation achieved, are discussed.

R. E. ESSERY

3204. Paper-chromatographic separations with cation-exchange papers. G. Illing (2, Grünerstr., Ludwigshafen). *Arch. Pharm., Berlin*, 1957, **290** (12), 581-582.—A mixture of lower aliphatic carboxylic acids, lactones, dicarboxylic acids, esters and anhydrides can be satisfactorily separated by paper chromatography with a cation-exchange paper containing 5% Dowex 50W (a sulphonated polyester resin). After neutralisation and saponification, the components are separated in *n*-propanol - water (3:1) and the chromatogram is developed with bromophenol blue.

M. H. SAWISTOWSKA

3205. Chromatography by liquid - liquid partition and liquid - liquid interface adsorption. H. van Duin (Netherlands Inst. for Dairy Res., Ede, Holland). *Nature*, 1957, **180**, 1473.—For liquid - liquid partition chromatography with columns, the relationship $\log R_i \approx \ln n$ holds for terms of homologous series, where n is the order of the term and R_i is the retention volume minus the volume of mobile phase in the column itself. Deviations from this have been investigated, with light petroleum, alone or mixed with CCl_4 or benzene, as non-polar phase, several polar solvents, alone or mixed, and homologous series of coloured derivatives of aliphatic alcohols, aldehydes, ketones, etc., with two types of silica gel to carry the stationary phase. If the gels were loaded over a certain limit, this relationship invariably held, and all the series tested could be separated. Loading with amounts of stationary phase less than the limit resulted in the simultaneous operation of liquid - liquid partition and liquid - liquid interface adsorption. The latter could be exploited as an independent chromatographic tool by using water as the stationary phase. It can also be applied in reversed-phase form and, because of the mild conditions, is suitable for the separation of labile substances.

R. E. ESSERY

3206. Some factors influencing the efficiency of gas - liquid partition chromatography columns. W. J. De Wet and V. Pretorius (Univ. of Pretoria,

S. Africa). *Anal. Chem.*, 1958, **30** (3), 325-329.—The effects of varying the carrier gas, the velocity of the carrier gas, the column temp., the particle size of the supporting medium, the density of the column packing and the amount of liquid phase used have been studied. The results are in agreement with theoretical considerations.

K. A. PROCTOR

3207. Use of mixed stationary liquids in gas-liquid chromatography. W. H. McFadden (Atomic Energy of Canada Ltd., Chalk River, Ont.). *Anal. Chem.*, 1958, **30** (4, Part I), 479-481.—Mixtures of mono- and di-bromoalkanes were separated by means of Tween 60 (polyoxyethylene sorbitan monostearate) and silicone oil as the stationary liquid phase on firebrick matrix. The equivalent behaviour of a two-stage chromatographic column and one prepared from an intimate mixture of the two packings is shown; both gave identical separations. Mixing the solvents before they were combined with the supporting material also gave a column with the same characteristics as a two-stage column. With silicone oil, the monobromoalkanes behaved as one class of compound and the dibromoalkanes as two classes. With the more polar Tween 60, the bromoalkanes behaved as several classes depending on the C-Br skeletal structure.

G. P. COOK

3208. A sensitive detector for gas chromatography. J. E. Lovelock (Nat. Inst. for Med. Res., Mill Hill, England). *J. Chromatography*, 1958, **1** (1), 35-46 (in English).—A simple apparatus is described, which employs the property possessed by argon, used as a carrier gas, of producing long-lived metastable atoms when irradiated with a 10-mC source of ^{90}Sr , these atoms causing ionisation of organic molecules by collision. The ionisation current ($\approx 10^{-8}$ amp.) is conveyed to a recorder by a d.c. amplifier modified for use with ionisation devices (Wellman and Lovelock, *J. Inst. Heating Ventilating Engrs.*, 1955, **22**, 421), an equal and opposite voltage being applied to the input so that the recorder reads zero with pure argon, and gives a positive deflection in the presence of organic compounds. Commercial argon can be used since the impurities do not interfere. The sensitivity can be varied over a wide range, and 2×10^{-12} mole of most organic compounds can be detected, the response being closely similar for different molecular species. The device is relatively insensitive to variations in temp., pressure, and rate of flow. When complete, it presents no external radiation hazard, but full precautions must be taken during assembly or dismantling. Details of performance are given, and the theory of operation is discussed.

R. E. ESSERY

3209. Electronic drop counter for ion-exchange chromatography. G. Coryn, A. Speecke and J. Hoste (Anal. Chem. Lab., Ghent Univ.). *Bull. Soc. Chim. Belg.*, 1957, **66** (11-12), 650-653 (in English).—In the photo-electric apparatus described, two switched circuits give automatic recording on a paper strip either of each drop or of every 50th one, with simultaneous counting of every drop on a mechanical register. Since, for a given solution, drop size is approx. constant over a range of elution speeds, the record obtained allows the elution constants to be determined.

S.C.I. ABSTR.

3210. A universal composition/anti-composition calculator for use in organic chemical analyses. W. D. Crow and Y. M. Greet (Div. of Ind. Chem., C.S.I.R.O., Melbourne, Australia). *Chem. & Ind.*, 1957, (50), 1618-1621.—An instrument for deriving empirical formulae from analytical results consists of a cylindrical multi-slide slide rule in which each slide makes one fixed calculation from its two scales. Each is a 1-cycle logarithmic scale, and they are offset by a factor equal to the wt. of the element or group for which the slide is constructed. The design and operation of the calculator are described and illustrated. Advantages claimed are (i) ease and rapidity of use, (ii) applicability to any combination of elements or groups, virtually without limits on mol. size, and (iii) visual scanning permits anticipation of possible formulae before they actually show in the marked limits; the degree of fit of each formula can then be determined quickly by an exact reversal of the anti-composition process.

W. J. BAKER

Optical

3211. A simple spectrophotometric measuring arrangement. G. Junghänel (Hochschule für Maschinenbau, Karl Marx Stadt, Germany). *Chem. Tech., Berlin*, 1957, **9** (3), 159-161.—The design and construction of a non-recording spectrophotometer capable of covering the range 2500 Å to 16 μ is fully described and illustrated. Difference, compensation and substitution methods of measurement are dealt with. In conclusion, examples are given of suitable light sources and instrument settings for the various spectral ranges. D. F. PHILLIPS

3212. Spectrochemical analysis by the evaporation method. S. Mandelstam (Phys. Inst., Acad. of Sci., USSR, Moscow). *Appl. Spectroscopy*, 1957, **11** (4), 157-158.—Samples are heated electrically in a graphite crucible to 1500° or higher. Impurities distil off and are collected on a water-cooled receiver electrode, which is subsequently arced or sparked. Enhanced sensitivities are thus obtained in spectra which are substantially free from radiation from the matrix element. A typical application is the determination of boron in triuranium octoxide. Sensitivities of several elements in refractory oxides or metallic samples are shown. P. T. BEALE

3213. A combination carbon-graphite electrode for d.c. arc analysis. J. W. Mellichamp and J. J. Finnegan (U.S. Army Signal Engng Lab., Fort Monmouth, New Jersey). *Appl. Spectroscopy*, 1957, **11** (4), 158-160.—The rapidity and sensitivity of the total combustion method may be increased by the use of a carbon crater for holding the sample. Difficulties in machining a carbon electrode to the required shape are overcome by use of a two-section electrode, which is readily drilled and in which the dimensional stability of the carbon and graphite rods used in its construction provides the necessary standardisation. P. T. BEALE

3214. Spectrochemical analysis of non-metallic samples. Pellet-spark technique with a multi-channel photo-electric spectrometer. W. H. Tingle and C. K. Matocha (Alcoa Res. Lab., New Kensington, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I),

494-498.—The procedure described, in which the sample is fused with lithium carbonate and boric oxide, pulverised, mixed with graphite, and pelleted, is independent of the sample origin or physical form. A low-inductance spark discharge is used for excitation. The method has been successfully applied to the rapid control and batch analysis of metallic elements present as major constituents in a non-metallic form, and gives a precision of 1 to 2% of the amount present. Limits of detection are given for 21 oxides. About 0.3 man-hour is required per sample on the batch process, and for control applications at least 6 elements can be determined in 30 to 40 min.

K. A. PROCTOR

3215. Time-resolved spectroscopy in spectrochemical analysis. A. Bardocz (Dept. for Spectroscopy, Central Res. Inst. of Physics, Hungarian Acad. of Sci., Budapest). *Appl. Spectroscopy*, 1957, **11** (4), 167-173.—Time-resolved spectra of transient spark discharges are obtained by combining an electronically controlled high-precision spark source with a rotating-mirror optical system. They provide information concerning excitation levels, pressure broadening, Stark broadening, intensity variations and self-absorption, which is useful in the selection of line pairs for spectrochemical analysis. A practical advantage of time-resolved spectra in analysis is the separation of the background, arising at the beginning of each spark, from the rest of the spectrum. An example is given of their application to the analysis of aluminium for impurities.

P. T. BEALE

3216. A spectrophotometer accessory for measuring absorption spectra of light-scattering samples. Spectra of dark-grown albino leaves and of adsorbed chlorophylls. J. H. C. Smith, K. Shibata and R. W. Hart (Carnegie Instn, Stanford, Calif., U.S.A.). *Arch. Biochem. Biophys.*, 1957, **72** (2), 457-464.—Details are given for the construction of an accessory incorporating an opal-glass screen for use with a Beckman DK-2 spectrophotometer. Improved spectra of thin solid samples are attained, and these are illustrated with the spectra of pure chlorophylls *a* and *b* adsorbed on filter-paper. W. H. C. SHAW

3217. Electrolytic lifting of films from metals for infra-red analysis. H. A. Szymanski and R. T. Conley (The Spectroscopy Lab., Canisius Coll., Buffalo, N.Y., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 552.—A method is described for producing films (1 in. long \times 0.5 in. wide) which are suitable for use in a potassium bromide pellet holder or between salt plates in a micro-cell. Excellent spectra have been obtained with films thicker or thinner than 0.00008 in.; at this thickness, fringe patterns caused some difficulty in obtaining satisfactory spectra.

K. A. PROCTOR

3218. The solvent effect in infra-red intensities. T. L. Brown (Noyes Chemical Lab., Univ. of Illinois, Urbana, U.S.A.). *Spectrochim. Acta*, 1957, **10** (2), 149-153.—Equations relating the intensities measured in solutions to one another and to the vapour intensity are derived and compared with experimental results. One equation which takes into account the shape of the solute molecule as well as the dielectric constant of the solvent can be used, at least qualitatively, to interpret a variety of solvent effects.

K. A. PROCTOR

3219. Method for the study of double and triple interferences in flame photometry. F. Burriel-Martí and J. Ramírez-Muñoz (Fac. of Sci., Univ., Madrid, Spain). *Inf. Quim. Anal.*, 1957, **11** (6), 169-188.—A method for the correction of interference effects in flame photometry is described. A straight-line correction curve is used in which the conversion factor is given as a function of the logarithm of the product of the ratio of interfering to the analysed element and their combined concentration. The method is developed to systems of three elements and in certain cases double corrections are required. Illustrative results for the systems Co-Mn-Cr (and binary combinations) and Ca-Na are shown.

L. A. O'NEILL

3220. Portable interferometer for fire-damp detection. L. Grupinski (Inst. für Optik und Spektroskopie, Adlershof, Berlin). *Chem. Tech., Berlin*, 1957, **9** (12), 725-727.—The design and construction of a portable gas interferometer are described, and tables of toxic and explosive properties of individual gases are presented.

J. L. PROSSER

Thermal

3221. An improved ebulliometer. C. Heitler (Dept. of Applied Chem., Northampton Coll. of Advanced Technol., London). *Analyst*, 1958, **83**, 223-229.—The ebulliometer described embodies a modified Cottrell pump and boiling cavity which reduce superheating to a minimum. Temp. is measured by means of a suitably aged thermistor of a type with a room-temp. resistance of $\approx 100,000$ ohms and a temp. coeff. of resistance of $\approx -4\%$ per $^{\circ}\text{C}$. The advantages of the thermistor are the minute heat capacity of its thermal element, its rapid response to small temp. changes, and its large resistance changes enabling a simple bridge circuit to be used for measurement. Mol. wt. can be determined rapidly, and results are given for a wide variety of compounds with mol. wt. from 100 to 314 determined in acetone or benzene. A. O. JONES

3222. Carbon and hydrogen combustion train (Pregl type). Microchemical apparatus. British Standards Institution (2 Park St., London). B.S. 1428; Part A1; 1958, 20 pp.—This Standard is a revised version of one published in 1950. It specifies the following components for the combustion train—pressure regulator, flow meter, pre-heater, U-tube, combustion tube, protective sheath, Bunsen burner, electric heater, constant-temperature bath, absorption tubes, guard tube, Mariotte bottle, and rubber tubing. Most components differ in details from those specified in B.S. 1428:1950. Silica is specified for the combustion tube and chloroprene (synthetic) rubber is now permitted as an alternative to natural rubber.

G. H. FOXLEY

3223. Differential thermal analysis apparatus for heating and cooling data. D. D. Williams, R. D. Barefoot and R. R. Miller (U.S. Naval Res. Lab., Washington, D.C., U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 492-494.—The versatile apparatus described is based on the concept of Rosenhain (*J. Inst. Metals*, 1915, **13**, 160) in which a vertical, heavy-walled metal tube 32 in. long is used to

establish a constant, reproducible temp. gradient. The sample holder, containing the thermocouples, is pulled in either direction through this tube at the rate required to produce the desired rates of temp. change. Individual runs require approx. 1 hr., but consecutive runs may be made immediately. Controlled-atmosphere work can be performed with simple modifications.

K. A. PROCTOR

Electrical

3224. A transistor-operated dispensing device for liquids. J. T. Stock and M. A. Fill (Dept. of Chem., Univ. of Connecticut, Storrs, U.S.A.). *Analyst*, 1958, **83**, 244-246.—The arrangement described consists essentially of a controllable timer used in conjunction with an electromagnet control valve. It serves for dispensing fixed vol. of liquids, e.g., indicators or stains, and for the filling of ampoules. Reagent additions can be progressively reduced as the end-point is approached, and the instrument can thus be used for routine or remotely controlled titrimetry.

A. O. JONES

3225. Instruments for measuring small quantities of sulphur dioxide in the atmosphere. W. G. Cummings and M. W. Redfern (Centr. Elect. Auth. Res. Lab., Leatherhead, Surrey, England). *J. Inst. Fuel*, 1957, **30**, 628-635.—An automatic recorder is described, in which the SO_2 is absorbed by a hydrogen peroxide reagent in a continuous countercurrent absorption column. The increase in conductivity of the reagent, due to the formation of H_2SO_4 , is measured. The recorder is intended for use over long periods of continuous operation on a fixed site. The second instrument described is a portable SO_2 meter. The SO_2 in the air reacts with a starch-iodine reagent in a countercurrent absorption column, and the amounts of light absorbed by the unchanged and the partially decolorised reagent are compared by photo-electric cells connected to a galvanometer. Both instruments are sensitive to 1 part of SO_2 in 100 million parts of air over the range 0 to 0.5 p.p.m.

A. R. PEARSON

3226. Apparatus for automatic controlled potential electrolysis using an electronic coulometer. L. L. Merritt, jun., E. L. Martin, jun., and Ram Dev Bedi (Dept. of Chem., Indiana Univ., Bloomington, U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 487-492.—The apparatus described can be used for performing electrolytic oxidations or reductions at controlled working-electrode potentials with automatic registration of the number of coulombs required. A constant current source supplies current to a large capacitor, which serves as the current source for the electrolysis cell. The time that the constant current is applied to the capacitor is measured.

K. A. PROCTOR

3227. Polarograph with direct recording of electrode potential. D. T. Sawyer, R. L. Pecsok and K. K. Jensen (Univ. of Calif., Riverside, U.S.A.). *Anal. Chem.*, 1958, **30** (4, Part I), 481-484.—The compact and versatile instrument described utilises an X-Y recorder for direct measurement of the electrode potential or applied voltage. The use of a third electrode gives an automatic correction for the iR drop across the cell. The performance of the instrument indicates an accuracy within ± 2 mV.

K. A. PROCTOR

3228. Twin electrodes in a.c. polarography. G. C. Barker and R. L. Faircloth (A.E.R.E., Harwell, England). *J. Polarographic Soc.*, 1958, **1** (1), 11-16.—Application of the twin-electrode technique to square-wave polarography, and methods of separation of overlapping waves are described.

H. F. W. KIRKPATRICK

3229. Mercury-pool electrode for continuous routine polarographic measurements. J. Závorka and F. Stráfelda (Inst. Anal. Chem., High-School Chem. Technol., Prague). *Chem. Listy*, 1957, **51** (12), 2374-2376.—The new arrangement enables mercury to be taken dropwise and automatically from the mercury layer; by means of the pressure of the flowing liquid (to be measured), mercury enters into an apparatus where it is purified and returned to the reservoir.

J. ZÝKA

3230. Electronic switch for differential polarography with dropping electrode. J. Krugers (Lab. Anal. Scheikunde, Univ., Amsterdam, Netherlands). *Chem. Weekbl.*, 1957, **53** (50), 672-674.—A circuit is described in which transistors are used, having the same properties as the rotating current commutator, but with reproducible contact-resistance and more dependable action. A square-wave generator is used.

P. RENTENAR

3231. Application of the hanging mercury drop to the determination of small quantities of various ions. Preliminary communication. W. Kemula and Z. Kublik (Univ. Warsaw, Poland). *Anal. Chim. Acta*, 1958, **18** (1-2), 104-111 (in French).—Oscillopolarography with a hanging mercury-drop electrode is applied to reversible and irreversible processes. Lithium is successfully determined at concn. $\approx 10^{-5} M$. In a second technique, oxidation currents are measured polarographically for amalgams already formed in the hanging drop. By this means, ion concn. of $\approx 10^{-5} M$ are determined.

J. H. WATON

3232. Use of the rotated dropping mercury electrode in polarographic analyses and amperometric titrations of micromolar solution. Nobuyuki Tanaka, Toshiko Koizumi, Teisuke Murayama, Mutsuo Kodama and Yasuhiko Sakuma (Dept. of Chem., Tohoku Univ., Sendai, Japan). *Anal. Chim. Acta*, 1958, **18** (1-2), 97-103 (in English).—The applicability of the rotating dropping mercury electrode in d.c. and a.c. polarography is considered, as well as its use as an indicator electrode in amperometry. In d.c. polarography, as little as 0.0008% of Pb in electrolytic zinc can be determined, but in a.c. polarography there is no advantage over the conventional dropping mercury electrode. In amperometry, micro amounts of Cu, Pb and Cd are successfully determined by titration with EDTA (disodium salt). Some characteristics of the rotating electrode are discussed.

J. H. WATON

3233. Factors to be considered in quantitative polarography with the rotated dropping mercury electrode. I. M. Kolthoff and Y. Okinaka (Sch. of Chem., Univ. of Minnesota, Minneapolis, U.S.A.). *Anal. Chim. Acta*, 1958, **18** (1-2), 83-96 (in English).—Factors that influence the limiting current at a rotating dropping mercury electrode are discussed. The half-wave potentials are of the same order as those observed at a conventional dropping mercury cathode. The rotating electrode is recommended for analyses where the concn. of the ions to be reduced is $< \approx 10^{-4} N$.

J. H. WATON

3234. Alternating current polarography. [I.] Improved experimental arrangement, examination of theory, and study of cadmium(II) reduction. H. H. Bauer and P. J. Elving (Univ. Mich., Ann Arbor, U.S.A.). *Anal. Chem.*, 1958, **30** (3), 334-341.—Theoretical and experimental factors are critically reviewed and methods of handling experimental and calculated data are suggested to facilitate the use of this technique. An experimental procedure is described for making adequate corrections for the effect of series resistances in the circuit.

II.] Determination of transfer coefficient of electrochemical processes. H. H. Bauer and P. J. Elving. *Ibid.*, 1958, **30** (3), 341-346.—The simple and rapid procedure described is a modification of that proposed by van Cakenberghe (*Bull. Soc. Chim. Belg.*, 1951, **60**, 3). Transfer coefficients can be determined with a precision of about ± 0.02 . The use of the procedure to measure transfer coefficients for the reduction of Cd^{II} at the dropping mercury electrode, in various media, is described.

K. A. PROCTOR

3235. Micro-analysis by oscillographic polarography. R. Kalvoda (Polarographic Inst., Czech. Acad. Sci., Prague). *Anal. Chim. Acta*, 1958, **18** (1-2), 132-139 (in German).—Oscillographic polarography is used in a comparative titration, in which the curve produced by adding a standard soln. of the ion being deposited to a comparison soln. is made to coincide with that given by the test soln. In another technique, material in the concn. range 10^{-4} to $10^{-3} M$ is determined oscillographically by measurement of the distance of the peak of the cut-in on the curve from the axis of potential. Micro-analysis of material in the range 10^{-3} to $10^{-2} M$ is carried out by the oscillographic determination of amalgams formed at a stationary mercury electrode.

J. H. WATON

3236. Current-scanning polarography at the dropping mercury electrode. Masayoshi Ishibashi and Taitiro Fujinaga (Anal. Chem. Lab., Fac. of Sci., Univ. Kyoto, Japan). *Anal. Chim. Acta*, 1958, **18** (1-2), 112-117 (in English).—Characteristics of polarograms obtained with the previously described current-scanning device (*cf. Anal. Abstr.*, 1957, **4**, 3516) are described.

J. H. WATON

3237. Square-wave polarography and some related techniques. G. C. Barker (A.E.R.E., Harwell, England). *Anal. Chim. Acta*, 1958, **18** (1-2), 118-131 (in English).—After a brief review of the theory of square-wave polarography, means of achieving greater sensitivity are discussed. The limiting factor in the sensitivity is the instability in the capillary response, and greater stability is attained with specially designed capillaries, or with a sessile drop electrode. The use of a rapid synchronised potential sweep or of a polarising pulse applied to the electrode once in the life of each drop will also extend the sensitivity. Newer techniques employ R.F. currents, both amplitude- and frequency-modulated. By these means, rapid electrode processes can be followed, and analyses performed in micro-cells with as little as 0.01 ml of soln.

J. H. WATON

3238. New techniques in radiochemical determinations using polarographic methods. D. L. Love (U.S. Naval Defense Lab., Anal. and Stand. Branch, San Francisco, Calif., U.S.A.). *Anal. Chim. Acta*, 1958, **18** (1-2), 72-80 (in English).—Rapid analysis and separation of radio-nuclides can be performed polarographically. The radio-isotopes, after reduction, are removed as amalgams. The presence or absence of inactive isotopes makes no difference to the amount of active isotope amalgamated.

J. H. WATON

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.	milli-equivalent	milli-equiv.
ampere	amp.	milligram	mg
Ångström unit	Å	millilitre	ml
anhydrous	anhyd.	millimetre	mm
approximate, -ly	approx.	millimicrogram	mμg
aqueous	aq.	millimolar	mM
atmospher-e, -ic	atm.	millivolt	mV
boiling-point	b.p.	minute (time)	min.
British thermal unit	B.Th.U.	molar (concentration)	M
calorie (large)	kg-cal.	molecul-e, -ar	mol.
calorie (small)	g-cal.	normal (concentration)	N
centimetre	cm	optical rotation	α _D
coefficient	coeff.	ounce	oz
concentrated	conc.	parts per million	p.p.m.
concentration	concn.	per cent.	%
constant	const.	per cent. (vol. in vol.)	% (v/v)
corrected	(corr.)	per cent. (wt. in vol.)	% (w/v)
crystalline	} cryst.	per cent. (wt. in wt.)	% (w/w)
crystallised		potential difference	p.d.
cubic	cu.	precipitate (as a noun)	ppt.
current density	c.d.	precipitated	pptd.
cycles per second	c/s	precipitating	pptg.
density	ρ	precipitation	pptn.
density, relative	d or wt. per ml	preparation	prep
dilute	dil.	qualitative, -ly	qual.
direct current	d.c.	quantitative, -ly	quant.
distilled	dist.	recrystallised	recryst.
ethylenediaminetetra-acetic acid	EDTA	refractive index	n _D
electromotive force	e.m.f.	relative band speed	R _r
equivalent	equiv.	relative humidity	r.h.
gram	g	revolutions per minute	r.p.m.
gram-molecule	mole	saponification value	sap. val.
half-wave potential	E _{1/2}	saturated calomel electrode	S.C.E.
hour	hr.	second (time)	sec.
hydrogen ion exponent	pH	soluble	sol.
infra-red	i.r.	solution	soln.
insoluble	insol.	specific gravity	sp. gr.
international unit	i.u.	specific rotation	[α] _D
kilogram	kg	square centimetre	sq. cm
kilovolt	kV	standard temp. and pressure	s.t.p.
kilowatt	kW	temperature	temp.
liquid	liq.	ultra-violet	u.v.
maxim-um, -a	max.	vapour density	v.d.
melting-point	m.p.	vapour pressure	v.p.
microgram	μg (not γ)	volt	V
microlitre	μl	volume	vol.
micromole	μmole	watt	W
micron	μ	wavelength	λ
milliampere	mA	weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	>	less than	<
not greater than	≥	not less than	≤
is proportional to	∝	of the order of, approximately	≈

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, e.g., Fe^{II}, Mo^V. Substances in the ionic state are represented by Na⁺, Fe³⁺, Fe²⁺, etc., for cations and by Cl⁻, SO₄²⁻, PO₄³⁻, etc., for anions.

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anhydrous	anhyd.	millimetre	mm
approximate, -ly	approx.	millimicrogram	m μ g
aqueous	aq.	millimolar	mM
atmospher-e, -ic	atm.	millivolt	mV
boiling-point	b.p.	minute (time)	min.
British thermal unit	B.Th.U.	molar (concentration)	M
calorie (large)	kg-cal.	molecul-e, -ar	mol.
calorie (small)	g-cal.	normal (concentration)	N
centimetre	cm	optical rotation	α_D^t
coefficient	coeff.	ounce	oz
concentrated	conc.	parts per million	p.p.m.
concentration	concn.	per cent.	%
constant	const.	per cent. (vol. in vol.)	% (v/v)
corrected	(corr.)	per cent. (wt. in vol.)	% (w/v)
crystalline	}cryst.	per cent. (wt. in wt.)	% (w/w)
crystallised		potential difference	p.d.
cubic	cu.	precipitate (as a noun)	ppt.
current density	c.d.	precipitated	pptd.
cycles per second	c/s	precipitating	pptg.
density	ρ	precipitation	pptn.
density, relative	d or wt. per ml	preparation	prep
dilute	dil.	qualitative, -ly	qual.
direct current	d.c.	quantitative, -ly	quant.
distilled	dist.	recrystallised	recryst.
ethylenediaminetetra-acetic acid	EDTA	refractive index	n_D^t
electromotive force	e.m.f.	relative band speed	R_F
equivalent	equiv.	relative humidity	r.h.
gram	g	revolutions per minute	r.p.m.
gram-molecule	mole	saponification value	sap. val.
half-wave potential	$E_{\frac{1}{2}}$	saturated calomel electrode	S.C.E.
hour	hr.	second (time)	sec.
hydrogen ion exponent	pH	soluble	sol.
infra-red	i.r.	solution	soln.
insoluble	insol.	specific gravity	sp. gr.
international unit	i.u.	specific rotation	$[\alpha]_D^t$
kilogram	kg	square centimetre	sq. cm
kilovolt	kV	standard temp. and pressure	s.t.p.
kilowatt	kW	temperature	temp.
liquid	liq.	ultra-violet	u.v.
maxim-um, -a	max.	vapour density	v.d.
melting-point	m.p.	vapour pressure	v.p.
microgram	μ g (not γ)	volt	V
microlitre	μ l	volume	vol.
micromole	μ mole	watt	W
micron	μ	wavelength	λ
milliampere	mA	weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	>	less than	<
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